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LATTICE-THEORY OF ALKALINE EARTH CARBONATES.

Part I. Lattice-Energy of Crystals of Aragonite Type and Their Thermo-Chemical Applications.

By B. Y. Oke.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received June 2, 1936.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Introduction.

Measurements[1] of the elasticity coefficients of Aragonite show a strong anisotropy. The two elasticity constants in perpendicular directions are in the ratio of 1 : 2. An attempt is made in this work to explain this anisotropy. According to the suggestion of Prof. M. Born the substance is assumed to be a polar compound composed of Ca^{++} and $(CO_3)^{--}$. The forces are the electrostatic attractions and repulsions of the charges and some other forces of the form $\frac{b}{r^n}$ which are usually assumed to account for the stability of the crystal.

Before taking up the actual calculations of the elasticity constants, it is necessary to calculate the total lattice-energy and to derive from this, with the help of the compressibility measurements, the value of n. In this paper we restrict ourselves to the evaluation of this n.

The lattice energy of the crystal is not a directly measurable quantity. It is, however, possible to construct chemical cyclic processes; after the manner of Born[2] and Haber,[3] in which this quantity enters along with other chemical quantities such as heat of sublimation, heat of formation, heat of ionisation, etc. The cyclic processes can be used to verify the theoretically calculated value of the lattice-energy, as well as to estimate the heats of certain chemical reactions.

---

[1] W. Voigt, *Ann. de Phy.*, 1907, **24**, 290.

[2] M. Born, *Verh. d. Deutsch Phys.*, 1919, **21**, 679.

[3] F. Haber, *Verh. d. Deutsch Phys.*, 1919, **21**, 750.

§1. Lattice-Energy of a Crystal.

The electrostatic potential of the lattice at a point $\vec{r}_{k'}$ of the lattice is called the " Selbs-potential " of the lattice at the point $\vec{r}_{k'}$ and is given by

$$\phi_{k'}(r_{k'}) = \sum_{l} \sum_{k}' \frac{e_k}{r^l_{kk'}} \quad .. \quad .. \quad .. \quad .. \quad (1, 1)$$

where $\sum_{l}$ denotes the summation over all the three cell-indices l_1, l_2, l_3 from $-\infty$ to ∞ and the dash over the summation sign Σ denotes that the index combination $l_1 = l_2, = l_3 = 0$ and $k = k'$ does not occur. e_k denotes the charge at the point k and $\vec{r}_{kk'}$ the radius-vector from k to k'.

The electro-static potential ϕ_0 at the points in a unit cell of the crystal is given by

$$\phi_0 = \sum_{k'} e_{k'} \phi_{k'}(r_{k'})$$

$$= \sum_{l} \sum_{kk'} \frac{e_k e_{k'}}{r^l_{kk'}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1, 2)$$

Let $\vec{a}, \vec{b}, \vec{c}$ be the " Grund-vectors " of the lattice and $\vec{a}', \vec{b}', \vec{c}'$ be the " Grund-vectors " of the reciprocal lattice so that

$$a' = \frac{1}{\Delta}[\vec{b} \times \vec{c}]\,;\; b' = \frac{1}{\Delta}[\vec{c} \times \vec{a}]\,;\; c' = \frac{1}{\Delta}[\vec{a} \times \vec{b}] \quad .. \quad (1, 3)$$

where $$\begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix} = \delta^3 = \Delta \quad .. \quad .. \quad .. \quad (1, 4)$$

We define a vector $\vec{q}^l$ by

$$\vec{q}^l = 2\pi (l_1 \vec{a}' + l_2 \vec{b}' + l_3 \vec{c}') \quad .. \quad .. \quad .. \quad (1, 5)$$

According to the method of Ewald[4] $\phi_{k'}(r_{k'})$ can be expressed as the sum of two expressions as follows

$$\phi_{k'}(r_{k'}) = e_{k'} \bar{\psi}(0) + \sum_{k}' e_k \psi(r_{kk'}) \quad .. \quad .. \quad .. \quad (1, 6)$$

where the dash over the summation sign denotes that the term $k = k'$ does not occur.

$\bar{\psi}(0)$ and $\psi(r_{kk'})$ are given by

$$\psi(r_{k'}) = \frac{4\pi}{\Delta} \sum_{l}' \frac{e^{i(\vec{q}^l \cdot r_{kk'})}}{|q^l|^2} \quad .. \quad .. \quad .. \quad .. \quad (1, 7)$$

---

[4] M. Born, "Ency. der Math. Wissen.," *Physik*, 3, 727.

and $$\bar{\psi}(0) = \bar{\psi}_1(0) + \bar{\psi}_2(0) \quad .. \quad .. \quad .. \quad .. \quad (1, 8)$$

where $$\bar{\psi}_1(0) = \frac{4\pi}{\Delta} \sum_l{}' \frac{e^{-\frac{1}{4\Sigma^2}|q^l|^2}}{|q^l|^2} - \frac{2\Sigma}{\sqrt{\pi}} \quad .. \quad .. \quad (1, 9)$$

and $$\bar{\psi}_2(0) = \sum_l{}' \frac{1 - \frac{2}{\sqrt{\pi}} \int_0^{\Sigma r^l} e^{-\alpha^2} d\alpha}{r^l} - \frac{\pi}{\Delta \Sigma^2} \quad .. \quad .. \quad (1, 10)$$

The introduction of this " Partition-factor " (Trennungstelle) Σ is the chief advantage of Ewald's method. The final result is independent of the choice of Σ; which may, therefore, be chosen in any suitable manner.

Substituting from (1, 6) in (1, 2)

$$\phi_0 = \bar{\psi}(0) \sum_{k'} e_{k'}{}^2 + \sum_{kk'} e_k e_{k'} \psi(r_{kk'}) \quad .. \quad .. \quad .. \quad (1, 11)$$

The electro-static energy density U_0 is given by $U_0 = \frac{1}{2\Delta} \phi_0$ .. (1, 12)

§2. *Electro-Static Energy Density of Aragonite and Similar Crystals.*

The crystals of calcium carbonate in the Aragonite form, as well as the crystals of Strontium and Barium-Carbonates, are ortho-rhombic. The " Grund-vectors " have the components

$$a_x = a, \quad b_y = b \quad c_z = c \quad .. \quad .. \quad .. \quad .. \quad (2, 1)$$

all other components being zero.

The values[5] of a, b, c, as found by X-ray analysis, are tabulated below in Ångström units.

TABLE I.

Substance	a	b	c
$CaCO_3$	4·94	7·94	5·72
$SrCO_3$	5·13	8·42	6·10
$BaCO_3$	5·29	8·38	6·41

The only surviving components of the " Grund-vectors " of the reciprocal lattice are

$$a'_x = \frac{1}{a}; \quad b'_y = \frac{1}{b}; \quad c'_z = \frac{1}{c} \quad .. \quad .. \quad .. \quad (2, 2)$$

[5] Wyckoff, *The Structure of Crystals*, 2nd edition, p. 273.

The vector $\overline{q^l}$ will have the components

$$\vec{q}^0 = 2\pi\left(\frac{l_1}{a}, \frac{l_2}{b}, \frac{l_3}{c}\right) \quad .. \quad .. \quad .. \quad .. \quad (2, 3)$$

(i) "Evaluation of $\bar{\psi}(0)$".—

Substituting the values of the components of $\overline{q^l}$ from (2, 3) in (1, 9) we get

$$\bar{\psi}_1(0) = \frac{4\pi}{\Delta} \sum_l \frac{e^{-\frac{\pi^2}{\Sigma^2}\left(\frac{l_1^2}{a^2} + \frac{l_2^2}{b^2} + \frac{l_3^2}{c^2}\right)}}{4\pi^2\left(\frac{l_1^2}{a^2} + \frac{l_2^2}{b^2} + \frac{l_3^2}{c^2}\right)} \quad .. \quad .. \quad (2, 4)$$

Taking $\Sigma = \frac{\pi}{b}$ .. .. (2, 5)

$$\bar{\psi}_1(0) = \frac{b^2}{\pi\Delta} \sum_l{}' \frac{e^{-\left(l_1^2\frac{b^2}{a^2} + l_2^2 + l_3^2\frac{b^2}{c^2}\right)}}{\left(l_1^2\frac{b^2}{a_2} + l_2^2 + l_3^2\frac{b^2}{c^2}\right)} - \frac{2\sqrt{\pi}}{b} \quad .. \quad (2, 6)$$

The expression under the sign of summation is rapidly converging and we need consider the first few terms only.

We tabulate below the results in detail for the case of Aragonite. In this we have $\left(\frac{b}{a}\right)^2 = 2{\cdot}58$ and $\left(\frac{b}{c}\right)^2 = 1{\cdot}926$. We write $2{\cdot}58\, l_1^2 + l_2^2 + 1{\cdot}926\, l_3^2 = \lambda_{l_1, l_2, l_3}$.

TABLE II.

l_1	l_2	l_3	λ_{l_1, l_2, l_3}	$e^{-\lambda_{l_1, l_2, l_3}}$	$\frac{e^{-\lambda_{l_1, l_2, l_3}}}{\lambda_{l_1, l_2, l_3}}$	$P(l_1, l_2, l_3)$	$P\frac{e^{-\lambda}}{\lambda}$
1	0	0	2·582	·0757	·0293	2	·0586
0	1	0	1	·3678	·3678	2	·7356
0	0	1	1·926	·1468	·0706	2	·1412
2	0	0	10·328	....	....	2	....
0	2	0	4	·0183	·0046	2	·0092
0	0	2	7·704	....	....	2	....
1	1	0	3·58	·0278	·0078	4	·0312
0	1	1	2·926	·0533	·0182	4	·0728
1	0	1	4·508	·0111	·0024	4	·0096
						Sum	1·0582

The 7th column gives the number of different combinations for the same numerical values of l_1, l_2, l_3; thus for $|l_1| = 1$; $|l_2| = 1$; and $l_3 = 0$ we have the following 4 combinations:

$$(1, 1, 0); \quad (-1, 1, 0); \quad (1, -1, 0); \quad (-1, -1, 0).$$

Hence

$$\bar{\psi}_1(0) = \frac{b^2}{\pi abc} 1{\cdot}0582 - \frac{2\pi}{\sqrt{\pi}\, b} \quad .. \quad .. \quad .. \quad (2, 7)$$

$$= \frac{{\cdot}71 \times 1{\cdot}0582 - 3{\cdot}544}{b} \quad .. \quad .. \quad .. \quad (2, 8)$$

Now

$$\bar{\psi}_2(0) = \sum_l{}' \frac{1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{\pi}{b} r'} e^{-a^2}\, da}{r'} - \frac{b^2}{\pi abc} \quad .. \quad .. \quad (2, 9)$$

The contribution of the first term containing the integral is negligible.

$$\therefore \quad \bar{\psi}_2(0) = -\frac{b/a \times b/c}{\pi\, b} \quad .. \quad .. \quad .. \quad .. \quad (2, 10)$$

$$= \frac{{\cdot}71}{b}$$

From (2, 8) and (2, 10)

$$\bar{\psi}(0) = \frac{{\cdot}71 \times {\cdot}0582 - 3{\cdot}544}{b} \quad .. \quad .. \quad .. \quad (2, 11)$$

$$= -\frac{3{\cdot}503}{b} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2, 12)$$

(ii) Evaluation of $\sum_{kk'} e_k\, e_{k'}\, \psi(r_{kk'})$.—

A unit cell of the crystal consists of 4 molecules of the carbonate. The calcium atoms are situated at

$$(0, 0, 2); \quad \left(\frac{a}{2}, \frac{b}{2}, 0\right); \left(0, \frac{b}{3}, \frac{c}{2}\right); \left(\frac{a}{2}, \frac{5b}{6}, \frac{c}{2}\right) \quad .. \quad .. \quad (2, 13)$$

and the CO_3 radicals at

$$\left(0, \frac{2b}{3}, \frac{c}{6}\right); \left(0, \frac{2b}{3}, \frac{2c}{3}\right); \left(\frac{a}{2}, \frac{b}{6}, \frac{c}{3}\right); \left(\frac{a}{2}, \frac{b}{6}, \frac{5c}{6}\right) \quad .. \quad (2, 14)$$

From (1, 7) and (2, 3)

$$\psi(r_{kk'}) = \frac{4\pi}{\Delta} \sum_l{}' \frac{e^{2\pi i\left(l_1 \frac{x_{kk'}}{a} + l_2 \frac{y_{kk'}}{b} + l_3 \frac{z_{kk'}}{c}\right)}}{4\pi^2 \left(l_1^2 \frac{1}{a^2} + l_2^2 \frac{1}{b^2} + l_3^2 \frac{1}{c^2}\right)} \quad .. \quad .. \quad (2, 15)$$

where $x_{kk'}$, $y_{kk'}$ and $z_{kk'}$ are the projections of $r_{kk'}$ on the three co-ordinate-axes.

Hence

$$\sum_{kk'} e_k e_{k'} \psi(r_{kk'}) = \frac{b^2}{\pi abc} \sum_{l}{}' \sum_{kk'} e_k e_{k'} \frac{e^{2\pi i\left(l_1 \frac{x_{kk'}}{a} + l_2 \frac{y_{kk'}}{b} + l_3 \frac{z_{kk'}}{c}\right)}}{\left(l_1^2 \frac{b^2}{a^2} + l_2^2 + l_3^2 \frac{b^2}{c^2}\right)} \quad .. \quad (2, 16)$$

Expressing the exponential as a cosine function this can be written as

$$\sum_{kk'} e_k e_{k'} \psi(r_{kk'}) = \frac{b^2}{\pi abc} \sum_{l'}{}' \sum_{kk'} \frac{2\cos\left(l_1' \frac{x_{kk'}}{a} + l_2' \frac{y_{kk'}}{b} + l_3' \frac{z_{kk'}}{c}\right)}{\left(l_1^2 \frac{b^2}{a^2} + l_2^2 + l_3^2 \frac{b^2}{c^2}\right)} \quad .. \quad (2, 17)$$

The dash over the l's denotes that if a certain set of values say $(\bar{l}_1, \bar{l}_2, \bar{l}_3)$ is taken, we need not consider the set $(-\bar{l}_1, -\bar{l}_2, -\bar{l}_3)$. Any other set like $(\bar{l}_1, -\bar{l}_2, -\bar{l}_3)$ or $(\bar{l}_1, -\bar{l}_2, \bar{l}_3)$ has however to be considered.

The co-ordinates of the 8 points in the cell are given in (2, 11) and (2, 12); from which the values of $x_{kk'}$, etc., are obtained. Substituting these and associating a charge $2e$ with each calcium atom and a charge $-2e$ with each CO_3 group, we obtain

$$\sum_{kk'} e_k e_{k'} \psi(r_{kk'}) = \frac{b/a\ b/c}{\pi\ b} 4e^2 \times 4 \sum_{l'}{}' \frac{F\{\cos(l_1', l_2', l_3')\pi\}}{l_1^2 \frac{b^2}{a^2} + l_2^2 + l_3 \frac{b^2}{c^2}} \quad .. \quad (2, 18)$$

where the function F is given by

$$\begin{aligned} F = {} & 2\cos(l_1+l_2)\pi + 2\cos l_3\pi + 2\cos\left(\frac{2}{3}l_2 + l_3\right)\pi + 2\cos\left(l_1 - l_2 + \frac{l_3}{3}\right)\pi \\ & + \cos\left(l_1 + \frac{5l_2}{3} + l_3\right)\pi + \cos\left(l_1 + \frac{l_2}{3} - l_3\right)\pi + \cos\left(l_1 - l_2 + \frac{4l_3}{3}\right)\pi + \cos\left(l_1 - l_2 - \frac{2}{3}l_3\right)\pi \\ & - \Big\{2\cos\left(\frac{4}{3}l_2 + \frac{l_3}{3}\right)\pi + 2\cos\left(\frac{2l_2}{3} - \frac{2l_3}{3}\right)\pi + \cos\left(\frac{4l_2}{3} + \frac{4l_3}{3}\right)\pi + \cos\left(\frac{2}{3}l_2 + \frac{5}{3}l_3\right)\pi \\ & + 2\cos\left(l_1 + \frac{l_2}{3} + \frac{2l_3}{3}\right)\pi\ 2\cos\left(l_1 - \frac{l_2}{3} - \frac{l_3}{3}\right)\pi + \cos\left(\frac{2l_2}{3} + \frac{l_3}{3}\right)\pi + \cos\left(\frac{4}{3}l_2 + \frac{2}{3}l_3\right)\pi \\ & + \cos\left(l_1 + \frac{l_2}{3} + \frac{5l_3}{2}\right)\pi + \cos\left(l_1 - \frac{l_2}{3} - \frac{4l_3}{3}\right)\pi + \cos\left(l_1 - \frac{l_2}{3} + \frac{2l_3}{3}\right)\pi \\ & + \cos\left(l_1 + \frac{l_2}{3} - \frac{l_3}{3}\right)\pi\Big\} \quad .. \quad (2, 19) \end{aligned}$$

As before we need consider only the first few terms of the series. Carrying out the summation we obtain

$$\sum_{kk'} e_k e_{k'} \psi(r_{kk'}) = -\frac{\cdot 71 \times 16e^2}{b} \times 5\cdot 598 \quad .. \quad .. \quad (2, 20)$$

Substituting the values from (2, 12) and (2, 20) in (1, 11) we get

$$\phi_0 = -\frac{e^2}{b}\,173{\cdot}608 \quad .. \quad .. \quad .. \quad .. \quad (2, 21)$$

From (1, 4) and (2, 1) we get

$$\delta^3 = abc \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2, 22)$$

Substituting the values for Aragonite from Table (I)

$$\delta = {\cdot}765\, b \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2, 23)$$

whence

$$\phi_0 = -\frac{e^2}{\delta}\,132{\cdot}8 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2, 24)$$

which may be written as

$$\phi_0 = -\,2\frac{e^2}{\delta}\,\alpha \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2, 25)$$

where $\alpha = 66{\cdot}4$ .. .. (2, 26)

The values of α for $SrCO_3$ and $BaCO_3$, by identical calculations, are found to be 66·58 and 66·87 respectively.

§3. *The Lattice-Energy.*

It has been already remarked that for the stability of the ionic crystals it is necessary to assume other forces besides the electro-static forces. With these forces, of the type $\frac{b}{r^n}$, the function ϕ_0 given in (2, 25) will be of the form

$$\phi_0 = -\,2\left(\alpha\frac{e^2}{\delta} - \frac{\beta}{\delta^n}\right) \quad .. \quad .. \quad .. \quad .. \quad (3, 1)$$

The "Lattice-Energy" per one mole of the substance is defined by

$$U = -\frac{1}{2z}\,N\,\phi_0 = \frac{1}{z}\,N\left(\frac{\alpha\,e^2}{\delta} - \frac{\beta}{\delta^n}\right) \quad .. \quad .. \quad (3, 2)$$

where z is the number of molecules per unit cell of the crystal, and N is Avogadro's number.

β and n can be determined from the equation[6]

$$\frac{\partial\phi_0}{\partial\delta} = 0 \text{ and } \frac{1}{18\delta}\frac{d^2\phi}{d\delta^2} = \frac{1}{\chi} \quad .. \quad .. \quad .. \quad .. \quad (3, 3)$$

where χ is the compressibility.

These equations give

$$\beta = \frac{\alpha\,e^2}{n}\,\delta^{n-1} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3, 4)$$

---

[6] M. Born, "Ency der Math. Wissen.," *Physik*, 3, 569, eqn. (90″).

and $$n = 1 + \frac{9}{\alpha e^2}\frac{\delta^4}{\chi} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3, 5)$$

whence equation (3, 2) can be written as

$$U = \left(1 - \frac{1}{n}\right) N \frac{a}{z}\frac{e^2}{\delta} \quad .. \quad .. \quad .. \quad .. \quad (3, 6)$$

If ρ is the density and M the molecular weight of the substance

$$\delta^3 N\rho = M_z \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3, 7)$$

so that equations (3, 5) and (3, 6) can be written in the more suitable form

$$n = 1 + \frac{9}{\alpha e^2 \chi}\left(\frac{M_z}{N\rho}\right)^{\frac{4}{3}} \quad .. \quad .. \quad .. \quad .. \quad (3, 8)$$

and $$U = \left(1 - \frac{1}{n}\right) \alpha e^2 \left(\frac{N}{z}\right)^{\frac{4}{3}} \left(\frac{\rho}{M}\right)^{\frac{1}{3}} \quad .. \quad .. \quad .. \quad (3, 9)$$

We tabulate below the results obtained.

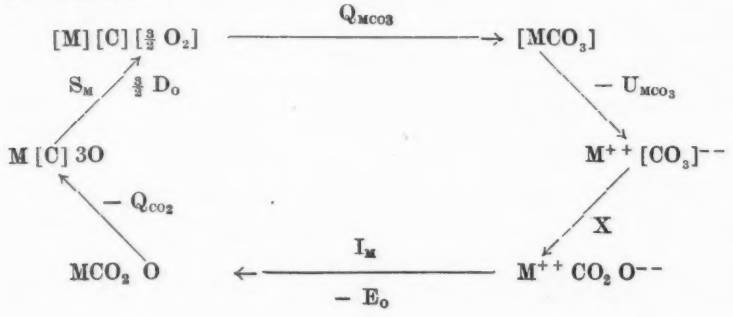
TABLE III.

Substance	a calculated	$\frac{1}{\chi \times 10^{12}}$ dynes/cm.^{2} experimental	M	ρ	n calculated	U in K.-cal. calculated
$CaCO_3$	66·40	·653	100·07	2·93	6·32	755·6
$SrCO_3$	66·58	·574	147·62	3·7	6·79	725·6
$BaCO_3$	66·87	·495	197·37	4·43	6·64	700·4

The values of χ are taken from Mellor's *Inorganic and Physical Chemistry*.

§4. *Thermo-Chemical Cycle.*

The "lattice-energy" is not a directly measurable quantity. We shall construct a thermo-chemical cycle, after the manner of Born and Haber so that the lattice-energy can be related to other measurable thermal data. The brackets denote the steady states. M stands for the alkaline earth metal.



where X is the heat of the chemical process

$$(CO_3)^{--} = CO_2 + O^{--} \quad .. \quad .. \quad .. \quad .. \quad (4, 1)$$

and

Q_{MCO_3} = Heat of formation of the carbonate.
U_{MCO_3} = Lattice-energy of the crystal.
I_M = Ionization energy of the metal.
E_O = Electronic affinity of oxygen.
Q_{CO_2} = Heat of formation of carbon dioxide.
S_M = Heat of sublimation of the metal.
D_O = Heat of dissociation of oxygen.

We have

$$Q_{MCO_3} - U_{MCO_3} + X + I_M - E_O - Q_{CO_2} + S_M + \tfrac{3}{2} D_O = 0 \quad .. \quad (4, 2)$$

Herein all the quantities except X and U are known. U is calculated in the last article. Hence we can use this equation to determine the value X. The agreement of the values of X from the cases of the 3 carbonates will verify the calculations of the " Lattice-Energy". From (4, 2) we get

$$X = B - A \quad .. \quad .. \quad .. \quad .. \quad .. \quad (4, 3)$$

where $B = U_{MCO_3} + Q_{CO_2}$

and $A = Q_{MCO} + I_M - E_O + S_M + \tfrac{3}{2} D_O \quad .. \quad .. \quad (4, 4)$

TABLE IV.

	$CaCO_3$	$SrCO_2$	$BaCO_3$	Source[7]
Q_{MCO_3}	270·8	279·2	283·0	1
I_M	413·0	383·9	349·1	3
$-E_O$	168·0	168·0	168·0	2
S_M	47·5	39·7	49·1	2
$\frac{3}{2} D_O$	88·8	88·8	88·8	1
A	988·1	959·6	938·0	..
U_{MCO_3}	755·6	725·6	700·4	Calculated
Q_{CO_2}	97·0	97·0	97·0	1
B	852·6	822·6	797·4	..
X	135·5	137·0	140·6	..

[7] [1] *Handbook of Chemistry and Physics*, Hodgman-Lange, 5th edition.
[2] G. Sherman, *Chemical Reviews*, 1932, **9**, 136 and 145.
[3] G. H. de Boer, *Electron Emission and Adsorption Phenomena*, 30.
The values are expressed in K. calories.

The agreement in the values of X is quite satisfactory. It is intended in the following paper to calculate the values of the elasticity coefficients in perpendicular directions. The knowledge of the value of 'n' will be found necessary in these calculations.

I wish to thank Prof. M. Born for his guidance in this work.

Summary.

The lattice-energies of crystals of Aragonite, of Strontium carbonate, and of Barium carbonate, which are all of the ortho-rhombic type, are calculated. Further the value of n is calculated with the help of the compressibility measurements. The lattice-energy values are verified by a thermo-chemical cyclic process.

Erratum.

"Ageing of Surfaces of Solutions—I." Page 11, Date of Receipt:—
For "June 2, 1936." *read* "February 28, 1936."

AGEING OF SURFACES OF SOLUTIONS—I.

The Study of Variation of Surface Tension of Solutions with Time by the Ring Method.*

By K. S. Gururaja Doss
and
Basrur Sanjiva Rao.
(*From the Department of Chemistry, Central College, Bangalore.*)

Received June 2, 1936.

The effect of the age of a surface on its surface tension was first noticed by Dupré.[1] It has since been studied by a number of workers.[2,3,4,5,6,7,8,9,22,23,24] The suitability of the ring method for such studies has been investigated in the present paper.

Experimental.

For studying the variation of surface tension with time the ring method is usually taken to be one of the best suited. *Cf.* Freundlich.[10] The technique of the ring method has been developed in full by Harkins and his co-workers.[11,12] The maximum pull exerted by a liquid on the ring when it is slowly withdrawn from the liquid surface, is measured by means of a chainomatic balance by Harkins and a torsion balance by du Noüy. Both these methods are too cumbersome to be worked in an isolated system. So, it was thought advantageous to use a quartz spring for the purpose.

An automatic device has been developed for the construction of helical springs of quartz. The quartz fibres were drawn in the usual way by pulling apart a quartz rod heated in the middle to the required temperature by means of an oxy-gas flame. When long and fine fibres were required, the heated rod was pulled out quickly by means of a falling weight. *Cf.* [13] By this method it was possible to get uniform fibres ten to twelve feet in length.

A silica tube about 1·2 cm. in diameter was given a screw motion by attaching it to the screw of a travelling microscope, which was moved by an electric motor geared down to give one revolution in three minutes. An oxy-air-gas flame played vertically down against the topmost portion of the tube. The fibre was fed horizontally through a capillary, the necessary

* Part of thesis on "Studies in Adsorption" submitted by K. S. G. Doss, in partial fulfilment of the requirements for the Degree of Master of Science of the Mysore University.

tension being given by a hanging weight. By this method one could readily get cornerless springs. In the case of the finest fibres the speed could be increased up to one turn per minute without any danger of overlapping.

The springs so prepared were calibrated by adding known weights and noting the extension through a vernier microscope reading to 0·01 mm. Within the range studied, Hooke's law was found to hold perfectly.

Four du Noüy rings were available; the best of them was selected. The circular stirrup was bent down to make it more or less elliptical. The stirrup was manipulated in such a way that the plane of the freely suspended ring remained perfectly horizontal; the presence of any tilt was detected by suspending the ring over a mercury surface and looking in between the ring and its image obtained by reflection at the mercury surface (Harkins has used a levelled gilt table). The ring was flamed before use.

The radii of the wire and the ring were measured by means of a Hilger "Photo-measuring Micrometer" reading to 0·001 mm. (kindly lent by Professor Venkatesachar of the Mysore University). The mean of twelve even diameters was chosen as the correct value.

The maximum pull was determined by making use of the apparatus shown in Fig. 1. It consisted of a U-tube with two bulbs. One of the limbs contained the spring carrying the ring. The liquid level in the limb was adjusted by suction or pressure through the other limb. The maximum pull was measured by means of a vernier microscope reading to 0·01 mm.

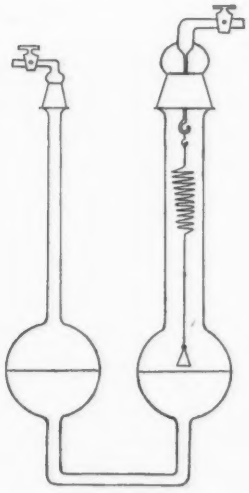


FIG. 1.

In order to standardise the procedure, the surface tension of toluene was determined. In calculating the surface tension from the value of the maximum pull the theories proposed by Cantor,[14] Lohnstein,[15] Lenard,[16] Tichanowsky,[17] and MacDougall,[18] are found to be unsatisfactory. Harkins and his co-workers[11,12] have determined the empirical corrections to be applied to the ring method. Freud and Freud[19] have given theoretical support to the empirical procedure. There has been a great deal of controversy as to whether one should make any allowance for the weight of the drops of the liquid, which cling to the ring, after the ring detaches itself from the liquid.[12,18,20] No such allowance has been made by Harkins in working out the corrections

to be applied. As long as one uses the corrections suggested by Harkins one should not make any allowance for the adherent drops. A value of 27·32 dynes per cm. was obtained for the surface tension of toluene at 30° C., while the value given in the *International Critical Tables* is 27·3 ± 0·1.

Variation of Surface Tension with Time.

A few alterations in the apparatus were necessary to study the variation of surface tension with time. As the surface of the liquid is to be disturbed to the least extent possible two modifications are found to be necessary: (*a*) The maximum pull should be determined without actually detaching the ring from the surface of the liquid; this was effected by employing a spring of smaller sensitivity (about 3 cm. per gm.). (*b*) The liquid level should be maintained very near the point of maximum pull so that the value

TABLE I.

Variation of Surface Tension with Time of an Aqueous Solution of Benzopurpurin (0·002 *Molar*).

Time in mins.	Extension for maximum pull in cm.			
	Exp. 1	Exp. 2	Exp. 3	Exp. 4
0	..	..	1·723	1·763
5	..	1·737	1·704	..
10	..	1·700	1·687	..
15	1·729	1·683	1·676	..
20	1·724	1·673	1·674	..
25	1·720	..	..	..
30	1·713	..	..	..
35	1·708	..	..	..
40	1·705	..	..	..
45	1·695	..	..	..
50	1·685	..	1·658	..
55	1·670	..	..	..
60	1·661	..	..	..
65	1·657	..	..	..
70	1·650	..	..	..
75	1·639	..	..	..
80	1·631	..	..	..
85	1·625	..	..	..
116	..	..	1·639	..
600	..	..	..	1·582

NOTE.—The reading corresponding to zero minutes is the one taken as quickly as possible after the formation of a fresh surface.

Extension of the spring per gram = 3.083 cm.

TABLE II.

Variation of Surface Tension with Time of Aqueous Solutions of Brilliant Green (0·0002 *Molar*).

Time in mins.	Extension for maximum pull in cm.			
	Exp. 1	Exp. 2	Exp. 3	Exp. 4
0	..	1·171	1·242	..
1	1·124	1·153	1·219	..
3·5	1·116	..	..	..
4·5	..	1·145	1·198	..
7	..	..	1·194	..
8	..	..	..	1·207
9	1·116	..	..	..
10	..	1·144	..	..
13	..	..	1·189	..
16	1·114	..	1·192	..
20	..	..	1·193	..
35	1·117	1·143	..	1·200
40	..	..	1·180	..
60	..	..	..	1·187
66	1·116	..	1·177	..
75	..	1·13	..	..
98	..	..9	..	1·185
144	..	1·135	..	1·177
183	..	..	..	1·174
273	..	1·125	..	..
296	..	1·129	..	..
348	..	1·127	..	..
468	..	1·119	..	..
600	..	..	1·137	..

NOTE.—Extension of the spring per gram = 2.366 cm.

for the pull is obtained by a very small movement of the liquid; for this purpose, a constant-head blow off was used to maintain the desired difference in level of liquid in the two arms of the U-tube. With this arrangement the liquid level could be maintained for several hours 0·1 mm. below the position of maximum pull without the least danger of the ring breaking off the liquid. Tables I and II illustrate the nature of the variation of the surface tension of aqueous solutions of benzopurpurin and brilliant green.

Water, benzene, toluene, and benzene soultions of (*a*) phenyl phenacyl ester of stearic acid and (*b*) sudan III did not show any change of surface tension with time. The liquids did not also exhibit the contact angle effect

(which is described later). It is found that the values for the maximum pull were not dependent to any appreciable extent on the speed at which the liquid was withdrawn from the ring.

Discussion.

The tables show that the results on the variation of surface tension with time are not reproducible. It was noticed that *the maximum pull differed according as the adjustment of levels was done by the advancing or the receding method.* This difference would exist only if the liquid has an angle of contact with platinum and the receding contact angle differs from the advancing angle. The existence of a contact angle is supported by the fact that the ring had a strong tendency to float on the solution. Moreover, a ring which was not completely immersed in the solution gave a reading of 1·197 as against 1·278 obtained when the ring was fully wetted by the liquid, both the readings being taken quickly. This difference (which is well beyond the limits of experimental error) shows clearly that the solution makes a contact angle with the material of the ring. The existence of a contact angle complicates the study of the effect of time on the surface tension. For, the absolute value of surface tension of a liquid having a contact angle cannot be easily computed (as the theory of the ring method becomes too complicated presenting certain mathematical difficulties in the calculation). Secondly, the angle of contact itself may change with time. For, if one expects a change in free energy with time of the liquid-vapour interface there is no reason why this should not be true of the solid-liquid interface. The ring method is usually taken to be one of the best suited for studying the variation of surface tension with time.[6,10,21,22] Johlin,[5] however, raises an objection on the grounds that a film of liquid is pulled out by the ring, leading to uncertainties in the measurements. But, as Harkins[12] has pointed out, this phenomenon in no way affects the measurements if one measures *the maximum pull.* Our own results show that one of the most serious objections for the use of the ring method in the study of variation of surface tension with time, is the existence of indefinite contact angles in such systems.

Summary.

An automatic device for the construction of quartz helical springs is described. The surface tension of toluene has been determined by the ring method employing a quartz helical spring for measuring the maximum pull. The effect of time on surface tension of several liquids has been studied and the results discussed. It is shown that the ring method is not suitable for the measurement of variation of surface tension with time.

We wish to thank Mr. M. R. Aswathanarayana Rao for his co-operation in the preparation of quartz springs.

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DISPERSION OF ACOUSTIC VELOCITY IN ORGANIC LIQUIDS.

By S. Parthasarathy.

(*From the Department of Physics, Indian Institute of Science, Bangalore.*)

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

The question of dispersion of acoustic velocity in liquids has been engaging the attention of experimental physicists for some time past. In the earlier days because of difficulties in realising very high frequencies experimentally, the problem remained unsolved. However, since the time when Pierce showed that by electrical circuits and a quartz crystal it was possible to produce supersonic vibrations, there have been attempts to determine velocities of sound at different frequencies. The earliest paper on the subject is one by R. W. Boyle and G. B. Taylor,[1] who working between the frequency range 43,000 to 600,000 c./s. reported a falling off of velocity at the higher frequency for water from 1510 m./s. to 1420 m./s. Since, however, a highly viscous oil examined by them did not show any dispersion, they reported results at a later date[2] of no detectable variation of sound velocity in water, in the range 29,000 to 527,000 c./s.

R. W. Wood, A. L. Loomis and J. C. Hubbard[3] have also reached a high frequency range. By the use of an acoustic interferometer, they measured the half wave-lengths and hence the velocity of sound in some liquids and found no variation in values. Their range was below a million cycles per second.

Later, B. Spakovskij[4] by using the same method experimented on water, alcohol, benzene, nitrobenzene, ethylene chloride, amyl acetate, ethyl acetate and acetone at two frequencies, roughly of 243,000 c./s. and 941,000 c./s. and reported no dispersion in these compounds.

When it was discovered in 1932, by Lucas-Biquard and Debye-Sears that velocities of sound could also be caculated at very much higher frequencies by the method of diffraction of light by ultrasonic waves (here the acoustic interferometer fails on account of very small wave-lengths of sound to be measured), Lucas and Biquard[5] tried to discover any dispersion in water by reaching as high a frequency as 20 millions per second. Within

limits of experimental error water was found to show no dispersion at all. Oyama,[6] employing the same method, has found that velocity for transformer oil decreased with increasing frequency, the range employed by him being from 464 Kc. to 20,000 Kc.

On account of the interest attaching to the subject, and also of a method now available which will carry one to very high ranges of frequency, it was thought desirable to pursue the subject further. In a paper[7] on the acoustic velocity in organic liquids, the author made a comparison of data available on the subject, from the audible range to $7 \cdot 32 \times 10^6$ c./s., which was the frequency employed by him, and reported no detectable dispersion. As however, it will be better to take compounds typical of each class than at random, this paper gives results of experiments on velocities made at two frequencies, namely, at about 7 and 20 mega-cycles per second carried out on 16 liquids representative of different families.

2. *Experimental.*

The oscillator set described in an earlier paper[7] was used to give frequencies at 7 and 20 millions a second.

The frequency of vibration was determined for every liquid by means of a precision wave-meter. The liquids used were pure and distilled.

3. *Results.*

Table I contains results of acoustic velocities determined at 20 and 7 Mc. The values at 7 Mc. have been taken from papers by the author published in the *Proceedings of the Indian Academy of Sciences*. In the last column is given the source from which the velocity has been taken. The second and third columns refer to temperature and the velocity in m./s. at 20 Mc., while the fourth and the fifth columns give the corresponding values at 7 Mc. Since the temperature coefficient of velocity is considerable, it is necessary to give the exact temperatures at which the velocities were determined experimentally.

It must be mentioned here that the two ranges of frequency were measured by a wave-meter, the resonances for these being obtained with two different coils, having ranges 28–40 meters and 15–28 meters respectively. However accurate an instrument may be, measurement with two coils is beset with uncertainties attendant on diverse calibration of the instrument. However, if allowance is made for the temperature variation of velocity for these compounds, correction due to this uncertainty appears to be negligible.

TABLE I.

Dispersion of Acoustic Velocities in Organic Liquids.

	Liquids	About $20 \cdot 0 \times 10^6$ c./s.		About $7 \cdot 3 \times 10^6$ c./s.		
		Temp. in ° C.	Velocity in meters per second	Temp. in °C.	Velocity in meters per second	Reference
	(*a*) *Hydrocarbons*					
1	Benzene ..	26°	1298	23°	1310	Part I
2	Toluene ..	25° ·5	1302	23°	1320	,,
3	*m*-xylene ..	26°	1309	23°	1334	,,
4	Cyclohexane ..	25° ·5	1248	23°	1257	,,
	(*b*) *Alcohol*					
5	Octylic alcohol (sec.)	26°	1297	26°	1302	Part V
	(*c*) *Ketones*					
6	Cyclohexanone ..	26°	1408	23° ·5	1441	Part I
7	Methyl cyclohexanone-*o* ..	26°	1352	25° ·5	1353	Part V
	(*d*) *Esters*					
8	Butyl acetate ..	25°	1192	26°	1179	Part III
9	Amyl formate ..	27°	1188	26°	1201	,,
	(*e*) *Ethers*					
10	Anisol ..	28°	1403	26°	1443	Part III
11	Resorcin dimethyl-ether ..	26°	1463	26°	1460	,,
12	*o*-cresol methyl ether	25° ·5	1402	26° ·5	1385	,,
	(*f*) *Halogen compounds*					
13	Chlorobenzene ..	26° ·5	1261	23°	1302	Part I
14	Butyl bromide (*n*)	26° ·5	1005	25° ·5	1016	Part IV
15	Acetylene dichloride (*cis*) ..	26° ·5	1009	25° ·5	1025	,,
	(*g*) *Base*					
16	α-Picoline ..	26°	1461	28°	1453	Part III

In the compounds investigated in this paper, no detectable dispersion is found, due allowance being made for temperature variation of acoustic velocity.

4. Discussion.

Recent experimental work on the dispersion of sound velocity in gases by Pierce,[8] Kneser,[9] Eucken[10] and his co-workers, Richards and Reid[11] and E. G. Richardson[12] and his co-workers has shown very clearly that in the case of polyatomic gases at least, there is dispersion followed by absorption of ultrasonic waves. The general explanation offered for such dispersion in gases is that a state of non-equilibrium is established in the medium which consists of particles having both translatory and rotatory motions owing to the passage of high frequency sound waves. Such an experimental fact in addition to giving much valuable information regarding the exchange of energy gives also an insight into the determination of the time of thermal relaxation for vibratory degrees of freedom.

From what has been said regarding the gases, it is undeniable that great interest attaches to the problem of acoustic dispersion in liquids. Since the liquid state is undefined, while we are fairly certain of the gaseous state, it is much more difficult to deal with the question of dispersion in liquids. However, to a first approximation, we can apply the laws of thermodynamics and determine where exactly to look for dispersion.

The well-known thermodynamic equation giving the relation between the two heat capacities is given by

$$C_p - C_v = \frac{T\alpha^2}{\beta_T \rho} \qquad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where C_p and C_v are the heat capacities at constant pressure and constant volume respectively;

T is the absolute temperature;

α is the coefficient of thermal expansion;

β_T is the isothermal compressibility;

and ρ the density of the liquid.

The velocity of sound and the ratio of the two heat capacities are given by

$$v^2 = \frac{\gamma}{\beta_T \rho} \quad \left(\text{since } \frac{C_p}{C_v} = \gamma = \frac{\beta_T}{\beta_\phi}\right) \qquad .. \quad .. \quad .. \quad (2)$$

here v is the velocity of sound in the liquid and γ is the ratio of heat capacities. (1) and (2) give

$$C_p = \frac{T\alpha^2 v^2}{v^2 \beta \rho - 1} \qquad .. \quad .. \quad .. \quad .. \quad .. \quad (3)$$

If we regard the equilibrium process and the non-equilibrium process due to the propagation of high frequency sound waves, to have, as well we may think when there is dispersion from an analogy in the gaseous phenomena, two different heat capacities C_{p1} and C_{p2}, then γ will be different for each state. Such a difference in C_{p1} and C_{p2} will give different values for the velocities of sound in a liquid, when we expect dispersion to occur.

Unfortunately we do not know much regarding the values of γ for liquids except those given by the author in a recent paper.[13] A knowledge of γ will give an idea of the vibratory degrees of freedom of the molecule and any possible dispersion could be looked for only in liquids possessing relatively few vibratory degrees of freedom. Then C_{p1} and C_{p2} will differ from each other to give dispersion of acoustic velocities.

In our experiments, we selected a number of compounds representative of different types and possessing also viscosity over a wide range, not very high enough for the quartz crystal to be completely damped. The results of experiments show no marked dispersion for any of the liquids studied.

It should be remarked here that for many liquids the acoustic velocities are not exactly identical. The temperatures at which the velocities were determined at the two frequencies were not the same and we know from the work of Freyer, Hubbard and Andrews[14] that the temperature coefficient of velocity is quite considerable for liquids. Secondly, a small uncertainty may be expected, as pointed out earlier, due to the employment of two coils of different ranges for determining the frequency of vibration. However, the uncertainty arising from the latter cause is seen to be small, as the small differences in the velocities at 7 and 20 megacycles are very well accounted for as mainly due to temperature variation of acoustic velocity.

Hence it is concluded that the different liquids investigated do not show any detectable dispersion up to the range of frequencies employed, namely, 7 and 20 million cycles per second.

I record my pleasant duty of thanking Sir C. V. Raman, Kt., F.R.S., N.L., for his keen interest in the work.

Summary.

Acoustic velocities at about 7×10^6 c./s. and 20×10^6 c./s. were determined in some hydrocarbons, one alcohol, ketones, esters, ethers, halogen substituted compounds and a base. No dispersion in velocity could be detected in any of these compounds.

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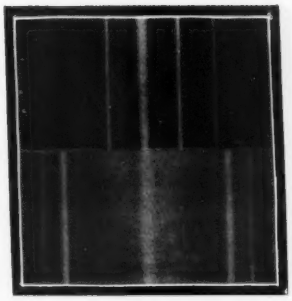

FIG. 1.

Diffraction Spectra in Butyl bromide (*n*)

(*a*) for 5461Å at $7{\cdot}00\times10^6$ c./s. (T=25°·5C.)

(*b*) for first order 4358Å and 5461Å at $19{\cdot}92\times10^6$ c./s. (T=26°·5C.)

COLLISION FREQUENCY IN SOLUTIONS.

By K. S. Gururaja Doss.

(From the Department of Chemistry, Central College, Bangalore.)

Received June 2, 1936.

Though it is usual, while working out the kinetics of reactions in solution, to employ the gas-kinetic equations for calculating the collision frequencies,[3] the exact meaning of a collision as referred to molecules in solution is not obvious. This is, in fact, one of the important questions suggested for general discussion at a symposium organised by the American Chemical Society.[1] The difficulty arises on account of the closeness of packing of the molecules which obtains in the liquid state of aggregation. An attempt is made in this paper to interpret the occurrence of collisions in view of the theory of liquids put forth by Wheeler.

According to Wheeler,[2] a liquid is composed of a number of simultaneously attracting and repelling force centres or molecules, each of which vibrates within a spherical space of diameter σ, which is kept free from other molecules by thermal motion of the occupying molecule. This picture has been useful in working out the relations between several of the physical properties of liquids. The study of the liquid state of aggregation has been approached from two sides. First, we have the relation of the liquid state of aggregation to the gaseous state, as is contained in the van der Waals' and other equations of state. Wheeler's theory, on the other hand, emphasises the points of similarity between the liquid and the solid states of aggregation. The conception of a collision arises from an analogy from the gaseous state, and we have in its place the vibration in Wheeler's theory. In effect, a complete vibration of a molecule can be considered as equivalent to two collisions taking place at the extreme positions of the vibrating molecule. Thus, it is of interest to derive expressions for the collision frequencies on the basis of Wheeler's theory and compare them with the gas-kinetic expressions for the same.

1. *The number of collisions between molecules of solute.*—The frequency of vibration ν, of a molecule in a liquid is given by

$$\nu = \frac{1}{\sqrt{2\pi}} \sqrt{\frac{RT}{M}} \cdot \frac{1}{\beta\sigma} \quad .. \quad .. \quad .. \quad .. \quad (i)$$

where ν = Frequency of vibration of a molecule in its associated space.

R = The gas constant per mole.

T = The absolute temperature.

M = The molecular weight.

β = The fractional amplitude of vibration in the associated space and σ = The diameter of the associated space.

To apply this equation for a solute molecule, it would be necessary to consider the possible way in which the diameter and the molecular weight of the solute molecule would affect the expression for ν. In the case of the simple solutes with not too high molecular weights these factors may not affect the order of ν. So, we shall assume that the vibration frequency of a solute molecule within its associated space is given by equation (i). The number of collisions per second encountered by a solute molecule with other molecules works out to be

$$2\nu = \frac{2}{\sqrt{2\pi}} \sqrt{\frac{RT}{M_1}} \cdot \frac{1}{\beta\sigma} \quad .. \quad .. \quad .. \quad .. \quad \text{(ii)}$$

Of this total number, a fraction $\frac{n_1}{n_2}$ will be the collision frequency of a solute molecule with the other solute molecules [n_1 = number of solute molecules per c.c. ; n_2 = total number of molecules per c.c.]. This comes out to be

$$2\nu \cdot \frac{n_1}{n_2} = \frac{n_1}{n_2} \cdot \frac{2}{\sqrt{2\pi}} \sqrt{\frac{RT}{M_1}} \cdot \frac{1}{\beta\sigma}.$$

The total number encountered by all the n_2 solute molecules becomes :

$$\frac{2\nu\, n_1^2}{n_2} = \frac{n_1^2}{n_2} \cdot \frac{2}{\sqrt{2\pi}} \sqrt{\frac{RT}{M_1}} \cdot \frac{1}{\beta\sigma}.$$

In this calculation, each of the collisions is counted twice : once, while the molecule is treated as a vibrating one and again when it is considered as bounding the asssociated space of another solute molecule. Thus, the correct collision frequency ${}_1Z_1$ is given by

$${}_1Z_1 = \frac{\nu\, n_1^2}{n_2} = \frac{n_1^2}{n_2} \cdot \frac{1}{\sqrt{2\pi}} \sqrt{\frac{RT}{M_1}} \cdot \frac{1}{\beta\sigma} \quad .. \quad .. \quad \text{(iii)}$$

In a dilute solution $n_2 \simeq$ number of solvent molecules per c.c. Thus, one can put

$$n_2\, \sigma^3 = \sqrt{2}.$$

Moreover, β is usually of the order of $\frac{1}{4\pi}$. Making these substitutions in (iii), we get

$${}_1Z_1 = \frac{n_1^2\, \sigma^3}{\sqrt{2}} \cdot \frac{1}{\sqrt{2\pi}} \sqrt{\frac{RT}{M_1}} \cdot \frac{4\pi}{\sigma}$$

$$= 2n_1^2\, \sigma^2 \sqrt{\frac{\pi RT}{M_1}}$$

which is identical with the corresponding gas-kinetic expression. It is to be noted that "σ" in the gas-kinetic expression is the collision diameter ;

but it is of the same order of magnitude as the diameter of the associated space.[4]

2. *The number of collisions between molecules of solute and molecules of solvent.*—In a dilute solution, the number of collisions encountered by a solute molecule with the solvent molecules is given by (ii). The total number ${}_1Z_2$ encountered by all the n_1 solute molecules becomes

$$ {}_1Z_2 = 2\nu n_1 = \frac{2\,n_1}{\sqrt{2\pi}} \sqrt{\frac{\overline{RT}}{M_1}} \cdot \frac{1}{\beta\sigma} \quad .. \quad .. \quad .. \quad \text{(iv)} $$

Let us express the same in terms of viscosity η. Wheeler has shown that

$$ \eta = \frac{8}{3N\beta\sigma^2} \sqrt{\frac{\overline{MRT}}{\pi}} \quad .. \quad .. \quad .. \quad .. \quad \text{(v)} $$

Combining (iv) and (v), we get

$$ {}_1Z_2 = \frac{3}{4\sqrt{2}} \cdot \frac{\eta N\sigma n_1}{M} \quad .. \quad .. \quad .. \quad .. \quad \text{(vi)} $$

The expression for ${}_1Z_2$, got by the application of the theory of Brownian movement, works out to be[5]

$$ \frac{3\pi}{2} \cdot \frac{\eta N\sigma n_1}{M} \quad .. \quad .. \quad .. \quad .. \quad .. \quad \text{(vii)} $$

Equations (vi) and (vii) are of the same form and differ by a factor of about 8·9. This is not surprising since both the equations have been derived by methods involving certain extrapolations. (In the extension of the theory of the Brownian movement to molecular motions, the extrapolation consists in assuming Stokes' law to hold for molecules.)

3. *The number of collisions between molecules of a solute and an interface.*—The collisions with a surface are produced by the oscillations of the molecules near the surface. Not all the vibrations (of the molecules present at the interface), however, contribute towards the collisions with the surface. It is only the vibrations perpendicular or nearly perpendicular to the surface that contribute towards the surface bombardment. Thus, the frequency of collisions of a solute molecule with the interface is equal to a fraction f, of the vibration frequency of the molecule. It is to be noted, that in the present case, a complete vibration corresponds to a single collision with the interface. All the solute molecules present within a distance σ from the interface can be considered as present at the interface. The number of such molecules per sq. cm. equals $n_1\sigma$. The frequency of collisions with the interface

$$ = Z = n_1\sigma f\nu = fn_1\sigma \frac{1}{\sqrt{2\pi}} \sqrt{\frac{\overline{RT}}{M}} \cdot \frac{1}{\beta\sigma} $$

$$ = \frac{f}{\beta} \cdot n \sqrt{\frac{RT}{2\pi M}}. $$

This equation is of the same form as the corresponding gas-kinetic expression and becomes identical with it when $f = \beta$, a relation which is but plausible.

Thus it is seen that the interpretation of a collision in solution in terms of Wheeler's theory of liquids, gives expressions for collision frequencies which turn out to be more or less the same as those got by the other methods and which have been employed with success for interpreting the kinetics of reactions in solution.

Summary.

An interpretation of a collision in solution is given on the basis of Wheeler's theory of liquids. The expressions for the collision frequencies based on this theory work out to be similar to those got by other methods and which have been used with success in the interpretation of kinetics of reaction in solution.

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ON THE VISIBILITY OF ULTRASONIC WAVES.

By P. Rama Pisharoty.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

Recently Raman and Nath[1] have developed a theory of the phenomenon of the diffraction of light by high frequency sound waves, discovered by Debye and Sears[2] in America and Lucas and Biquard[3] in France. The essential idea of the theory is that the phenomenon depends on the corrugated form of the wavefront of the transmitted beam. The sinusoidally corrugated form of the wavefront is obtained by considering the phase changes accompanying the traversing beam and it is assumed that the amplitude is constant throughout. Now Hiedeman,[4] Bär,[5] and Lucas[6] have experimentally established the visibility of the progressive ultrasonic waves using a microscope and a Kerr cell. Raman and Nath have explained this by postulating amplitude changes as well on the emerging wavefront, their general wave-function being obtained as a general solution of the partial differential equation governing the propagation of light in a medium filled with sound waves.

We will consider in this paper how a beam of constant amplitude but having a simple harmonically corrugated wavefront builds up periodic amplitude changes as well, when propagated through distances small compared with the width of the wavefront,—small enough as not to allow the different plane components to separate out.

2. Theory.

The direct method to determine the form of the constant amplitude corrugated wavefront when propagated through a short distance would be to find the diffraction pattern on a plane parallel to the original mean wavefront and at a finite distance from it by the usual Fresnel procedure. But as the integration involved is complicated an alternative method is adopted. The corrugated wavefront is resolved into an infinite number of plane wavefronts having different inclinations to the mean wavefront. Then the effect of each of these plane waves at a point on the required plane is calculated and the effects summed up for all the plane components.

(*a*) *Resolution of the corrugated wavefront into plane waves.*—

Let us take the X axis along the direction in which the phase change periodically, the Y axis parallel to the lines of constant phase, and the Z axis along the direction of propagation of the light beam.

A simple harmonically corrugated wavefront is then represented by

$$Ae^{2\pi i\nu t}\, e^{\frac{2\pi}{\lambda}\, i\left(a \sin \frac{2\pi}{\lambda^*} x\right)}$$

where ν is the frequency of the light waves,
λ is its wave-length in the medium,
a is the amplitude of the phase variation,
and λ^* is the wave-length of the phase variation.

The factor

$$e^{\frac{2\pi i}{\lambda}\left(a \sin \frac{2\pi}{\lambda^*} x\right)}$$

may be written as

$$\cos (v \sin bx) + i \sin (v \sin bx)$$

where $v = \dfrac{2\pi a}{\lambda}$ and $b = \dfrac{2\pi}{\lambda^*}$.

Using the well-known Bessel expansions for

$$\cos (v \sin bx) \text{ and } \sin (v \sin bx)$$

we have,

$$\cos (v \sin bx) + i \sin (v \sin bx)$$

$$= 2 \sum_0^{\infty}{}' \mathrm{J}_{2r} (v) \cos 2rbx + 2\, i \sum_0^{\infty} \mathrm{J}_{2r+1} (v) \sin 2r + 1\, bx \qquad .. \quad (1)$$

$$= \Sigma' \mathrm{J}_{2r} (v) \{e^{i2rbx} + e^{-i2rbx}\} + \sum_0^{\infty} \mathrm{J}_{2r+1} (v) \{e^{i\overline{2r+1}\, bx} - e^{-i\overline{2r+1}\, bx}\}$$

Remembering that $\mathrm{J}_n (v) = (-1)^n \mathrm{J}_{(-n)} v$,
we may put the above as

$$\sum_{-\infty}^{+\infty} \mathrm{J}_n (v)\, e^{inbx}$$

Then the corrugated wavefront is

$$\sum_{-\infty}^{+\infty} \mathrm{J}_n (v)\, e^{inbx}\, e^{2\pi i\nu t}$$

$$= \sum_{-\infty}^{+\infty} \mathrm{J}_n (v)\, e^{\frac{2\pi i}{\lambda}(\nu t + np x)} \qquad .. \quad .. \quad (2)$$

where $$p = b/\frac{2\pi}{\lambda} = \frac{\lambda}{\lambda^*} \qquad .. \quad .. \quad .. \quad .. \quad (3)$$

The interpretation of this expression is that a sinusoidally corrugated wavefront is equivalent to an infinite number of plane waves of amplitudes $J_n(v)$ and inclinations to the mean wavefront given by $\text{Sin}^{-1}(-np)$.

(*b*) *The evaluation of the diffraction effects on a parallel plane.*—

To evaluate the effect of the corrugated wavefront at a point P in a plane parallel to the *xy*-plane and at a distance Z from the *xy* plane, we propose to calculate the effect of each plane wave component separately and then to sum up the effect.

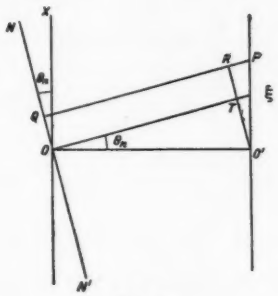

FIG. 1.

Consider a single plane wavefront NON′ having an inclination θ_n with the *xy*-plane. To consider its effect at P, a point on the required plane, drop the normal PQ on to NON′.

$$\text{Now PQ} = \text{QR} + \text{RP} = \text{OT} + \text{RP}$$
$$= Z \cos \theta_n + \xi \sin \theta_n.$$

Therefore the vibration at P due to the wavefront NON′

$$= J_n(v) \cos \frac{2\pi}{\lambda} (Vt - Pq).$$

$$= J_n(v) \cos \frac{2\pi}{\lambda} (Vt - Z \cos \theta_n - \xi \sin \theta_n).$$

Here $J_n(v)$ is the amplitude of the nth order plane wave, and θ_n its inclination given by the relation

$$\sin \theta_n = -np = -n \frac{\lambda}{\lambda^*}.$$

Hence the resultant vibration at P due to all the components

$$= \sum_{-\infty}^{+\infty} J_n(v) \cos \frac{2\pi}{\lambda} (Vt - Z \cos \theta_n - \xi \sin \theta_n) \quad .. \quad .. \quad (4)$$

$\cos \theta_n$ is always of the same sign, while $\sin \theta_n$ changes sign with n. $J_n(v)$ changes sign with n when n is odd. To take these into consideration the

series is split up into four sub-series, two for positive and negative even values of n, and two for the corresponding odd values of n. Simplyfying on these lines and substituting for θ_n, the resultant vibration at P is given by

$$2\,\Sigma'\,J_{2r}(v)\cos\frac{2\pi}{\lambda}\,(Vt-Z\,\sqrt{1-\overline{2r}^2\,p^2})\cos\frac{2\pi}{\lambda}\,\xi\cdot 2rp$$

$$+\,2\,\Sigma\,J_{2r+1}(v)\sin\frac{2\pi}{\lambda}\,\{Vt-Z\,\sqrt{1-\overline{2r+1}^2\,p^2}\}\sin\frac{2\pi}{\lambda}\,\xi\cdot\overline{2r+1}\,p.$$

$$=A\cos\frac{2\pi}{\lambda}\,Vt+B\sin\frac{2\pi}{\lambda}\cdot Vt \qquad \text{(say)} \qquad .. \qquad .. \qquad (5)$$

Then

$$A=2\,\Sigma'\,J_{2r}(v)\cos\frac{2\pi}{\lambda}\cdot Z\,\sqrt{1-\overline{2r}^2\,p^2}.\ \cos\left(\frac{2\pi}{\lambda}\cdot\xi\cdot 2rp\right)$$

$$-\,2\,\Sigma\,J_{2r+1}(v)\sin\frac{2\pi}{\lambda}\,Z\,\sqrt{1-\overline{2r+1}^2\,p^2}.\ \sin\left(\frac{2\pi}{\lambda}\,\xi\cdot\overline{2r+1}\,p\right) \quad (6)$$

and

$$B=2\,\Sigma'\,J_{2r}(v)\sin\frac{2\pi}{\lambda}\,Z\,\sqrt{1-\overline{2r}^2\,p^2}.\ \cos\frac{2\pi}{\lambda}\cdot\xi\cdot 2rp.$$

$$+\,2\,\Sigma\,J_{2r+1}(v)\cos\frac{2\pi}{\lambda}\,Z\,\sqrt{1-\overline{2r+1}^2\,p^2}.\ \sin\frac{2\pi}{\lambda}\cdot\xi\cdot\overline{2r+1}\,p\ ..\quad (7)$$

The intensity I at the point P is given by the equation

$$I=A^2+B^2$$

when $Z=0$, or a small multiple of λ,

$$A=2\,\Sigma'\,J_{2r}(v)\cos\frac{2\pi}{\lambda}\cdot\xi\cdot 2rp=\cos(v\sin b\xi)$$

and $$B=2\,\Sigma\,J_{2r+1}(v)\sin\frac{2\pi}{\lambda}\cdot\xi\cdot\overline{2r+1}\,p=\sin(v\sin b\xi)$$

since $$\frac{2\pi p}{\lambda}=\frac{2\pi}{\lambda}\cdot\frac{\lambda}{\lambda^*}=\frac{2\pi}{\lambda^*}=b.$$

Hence $I=A^2+B^2=1$.

Therefore the expressions give a corrugated wavefront of constant amplitude when it is propagated only through a few wave-lengths of light.

But the expressions for A and B cease to be simple when Z is a large multiple of λ.

Let us put

$$\tfrac{1}{4}\cdot\frac{(\lambda^*)^2}{\lambda}=d.$$

This corresponds to a distance of a half-a-cm., when λ is taken as 5000 Å.U. and λ^*, the wave-length of the corrugations to be 0·01 cm., the value corresponding to the usual ultrasonic wave-lengths in liquids.

When $Z=d$, $\cos\frac{2\pi}{\lambda}\,Z\,\sqrt{1-n^2p^2}$ and $\sin\frac{2\pi}{\lambda}\,\sqrt{1-n^2p^2}$, assume simple values of $\pm\,1$ or 0.

The following table gives the values of A and B for definite values of Z, the distance of propagation :—

Z	A	B
0, $2d$, $4d$, etc.	$\cos(v \sin b\xi)$	$\pm \sin(v \sin b\xi)$
d, $5d$, $9d$, etc.	$\cos(v \sin b\xi) + \sin(v \sin b\xi)$	$\sin(v \sin b\xi)$
$3d$, $7d$, $11d$, etc.	$\cos(v \sin b\xi) - \sin(v \sin b\xi)$	$\sin(v \sin b\xi)$

Fig. 2 represents the values of $A^2 + B^2$, *i.e.*, the intensity for the various values of Z, for two different cases $v = 1$ and $v = 2$.

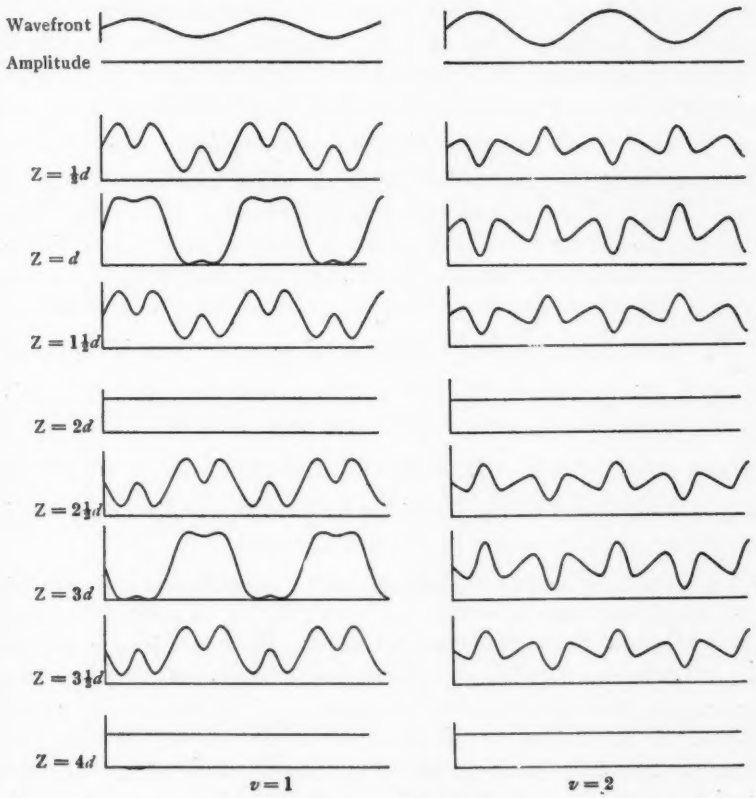

FIG. 2.

For values of Z equal to fractional values of d, there are amplitude changes as well as phase changes on the wavefront.

When $$Z = n\frac{d}{2},$$

$$A = \cos(v \sin b\xi) + \sin\left(\frac{n\pi}{4}\right).\sin(v \sin b\xi)$$

and $$B = \sin\left(\frac{n\pi}{4}\right).\sin(v \sin b\xi),$$

for values of v not greater than 3. These cases also are represented in Fig. 2.

We see therefore that a simple-harmonically corrugated wavefront develops amplitude changes on it when propagated. The number of amplitude changes is equal to that of the initial corrugations only when the depth of the corrugations is small. As the depth of the corrugations increase the number of the amplitude changes, corresponding to each wave-length of the corrugation, also increases. This is to be expected, for, when the depth of the corrugations increase more and more of the plane wave components assume importance and give rise to more interference bands.

3. Application of the Theory to Ultrasonics.

The visibility of the progressive ultrasonic waves observed through a microscope using a Kerr cell, may be explained by these deductions. The microscope is focussed on one of the planes at which the corrugated wavefront has developed into an amplitude grating. The fringes ought to disappear when the microscope is pushed in or out through a distance $d = \frac{1}{4}\frac{(\lambda^*)^2}{\lambda}$. (This corresponds to a distance of 0·5 cm. when λ^* is taken as 0·01 cm. and λ as 5000 Å.U.) But if it is moved through double this distance the fringes should appear again, but with a lateral displacement of $\frac{\lambda^*}{2}$ of the whole pattern. If, on the other hand, there are amplitude changes as well impressed on the wavefront on its emergence from the sound field, the pattern should continue to be visible throughout.

With a stationary ultrasonic field we have a pulsating wavefront and the above amplitude changes would be practically or completely washed out. The observers do report the visibility of a stationary sound field also. This shows that there are amplitude changes as well on the emerging wavefront before its further propagation. This may be due to the superposition of the Brillouin[7] effects on the phase change corrugations of the emerging wavefront. An experimental evidence for such a superposition of the two effects is given by Parthasarathy,[8] in a recent paper.

4. Applicability of the 'Schlieren' Method.

Lord Rayleigh[9] has given the theory of the Foucoult's test, *i.e.*, the Schlieren method, for the detection of small path differences. In Fig. 3, A represents the lens, with its rectangular aperture, which brings parallel rays to a focus. In the focal plane B there are two adjustable screens with horizontal edges and immediately behind is the objective of a small telescope.

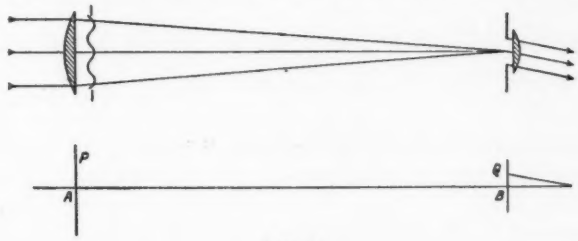

FIG. 3.

The rays from the various points Q of the second aperture which unite at a point in the focal plane of the telescope may be regarded as a parallel pencil inclined to the axis at an angle ψ. P is a point in the first aperture. $AP = x$, $BQ = \xi$, and $AB = f$. Let the additional path retardation operative at A, giving a corrugated form to the wavefront be denoted by R, a function of x. Thus if V be the velocity of propagation of light and $k = \frac{2\pi}{\lambda}$, the vibration at a point ξ of the second aperture will be represented by

$$\int dx \sin k\left(Vt - f - R + \frac{x\xi}{f}\right)$$

Or, if $\frac{x}{f} = \theta$, by

$$\int d\theta . \sin k\,(Vt - f - R + \xi\theta) \qquad .. \qquad .. \qquad (8)$$

When we proceed to enquire what is to be observed at an angle ψ, we have to consider the integral

$$\int_{-\xi}^{+\xi} d\xi \int_{-\theta}^{+\theta} d\theta \sin k\,\{Vt - f - R + \xi\,(\theta + \psi)\} \qquad .. \qquad .. \qquad (9)$$

For a simple-harmonically corrugated wavefront, we have the function R given by the relation

$$R = a \sin \frac{2\pi}{\lambda^*} x = a \sin \frac{2\pi f}{\lambda^*} \theta \qquad .. \qquad .. \qquad .. \qquad .. \qquad (10)$$

where λ^* is the wave-length of the corrugations, and a is the amplitude of the corrugations.

It is more convenient to carry out first the integration with respect to ξ.

Using the expansions for cos (v sin bx) and sin (v sin bx) given by the equation (1) and carrying out the second integration as well, we find the resultant vibration given by

$$A \sin (Vt - f) - B \cos (Vt - f) \quad .. \quad .. \quad .. \quad .. \quad (11)$$

where

$$A = \Sigma' J_{2r}(ka) \cos 2rb\psi \{si (k\xi + 2rb) (\theta + \psi) + si (k\xi + 2rb) (\theta - \psi) + si (k\xi - 2rb) (\theta + \psi) + si (k\xi - 2rb) (\theta - \psi)\} \quad .. \quad .. \quad (11a)$$

and

$$B = \Sigma J_{2r+1}(ka) \sin (2r+1) b\psi \{si (k\xi + \overline{2r+1}b) (\theta + \psi) + si (k\xi + \overline{2r+1}\, b) (\theta - \psi) + si (k\xi - \overline{2r+1}\, b) (\theta + \psi) + si (k\xi - \overline{2r+1}\, b) (\theta - \psi)\} \quad .. \quad ((11b)$$

$J_n (ka)$ represents the Bessel function of the nth order. $k = \frac{2\pi}{\lambda}$, $b = \frac{2\pi f}{\lambda^*}$ and 2ξ is the width of the second aperture which is symmetrically situated with respect to the geometrical focus.

$$si\ x = \int_0^x \frac{\sin x}{x}\, dx.$$

The dash over the summation in A represents that the coefficient of the first term of the series is half of those of the rest.

As already shown in Section 3, the corrugated wavefront can be resolved into a number of plane waves having inclinations α to the mean wavefront given by

$$\sin \alpha = \pm\, n \frac{\lambda}{\lambda^*}.$$

The series in A and B continue only as long as $k\xi > nb$. For, when $k\xi < nb$ the corresponding terms in both the series vanish, since si (x) when x is large is $\frac{\pi}{2}$ and si $(-x) = -\frac{\pi}{2}$.

Now, $k\xi > nb$

$$i.e., \frac{2\pi}{\lambda} \xi > n. \frac{2\pi f}{\lambda^*}$$

$$i.e., \frac{\xi}{f} > n \frac{\lambda}{\lambda^*}$$

means that the nth order spectrum is admitted into the second aperture.

When a large number of spectra are admitted into the second aperture, A and B are to be continued to a large number of terms. Then

$$A = 2\pi \Sigma' J_{2r}(ka) \cos 2rb\psi = \pi \cos (ka \sin b\psi)$$

and $$B = 2\pi \Sigma J_{2r+1}(ka) \sin \overline{2r+1}\, b\psi = \pi \sin (ka \sin b\psi);$$

so that $A^2 + B^2 =$ a constant.

Therefore the intensity is uniform and the aperture at A appears uniformly illuminated. Uniform illumination is the result even when one half of the second aperture is cut out.

If on the other hand, the second aperture is just large enough to admit the direct and the first order of lateral spectra only, we have the intensity distribution with ψ given by

$$I \propto \{J_0 (ka)\}^2 + \{2J_1 (ka) \sin b\psi\}^2.$$

Here the intensity varies with ψ. Even in this case the visibility is in general poor because of the constant term $\{J_0 (ka)\}^2$. If the second orders are also admitted by slightly increasing the second aperture, a cosine term also comes in and the visibility practically ceases.

Thus we find that the ' Schlieren ' effects of a corrugated wavefront are poor. This is in accordance with Lord Rayleigh's statement that continuous phase changes are not easily detected by the Foucoult's test.

The author wishes to thank Sir C. V. Raman, Kt., F.R.S., N.L., for the suggestion of the problem and the valuable help during its solution.

5. *Summary.*

The diffraction effects caused by a simple-harmonically corrugated wavefront when propagated through distances small compared with the extent of the wavefront—small enough as not to allow the various orders of spectra to separate out, are considered. Such a wavefront on propagation develops at a definite distance $d = \frac{1}{4} \frac{(\lambda^*)^2}{\lambda}$, into one of uniform phase but having periodic *amplitude* changes on it. On further propagation to twice this distance it becomes a corrugated wavefront again. At intermediate stages there are both amplitude and phase changes. At a distance $\frac{3}{4} \frac{(\lambda^*)^2}{\lambda}$ the pattern is similar to that at d but is displaced laterally through $\frac{\lambda^*}{2}$. It is suggested that the visibility of the progressive ultrasonic waves observed with a microscope and a Kerr cell is due to these amplitude changes brought about by the propagation of a purely corrugated wavefront. Lord Rayleigh's theory of the ' Foucoult's test ' is applied to such a wavefront and it is shown that its Schlieren effects would be poor.

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MAGNETISM AND COLD-WORKING IN METALS.

Part I. Polycrystals.

By Dr. S. Ramachandra Rao.
(*From the Department of Physics, Annamalai University.*)

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1. *Introduction.*

The systematic and comprehensive investigations of Honda[1] and Owen[2] on the susceptibilities of some sixty elements enabled a clear elucidation of the magnetic properties of metals and non-metals to be made for the first time. Their measurements were extended over considerable ranges of temperature and the most careful precautions were taken to correct for the presence of ferromagnetic impurities in the specimens. Based on these and the results of other investigators in more recent years, general attempts have been made to account for the magnetic properties of metals from a theoretical point of view.[3]

The problem of the metallic state is indeed very complicated. In a general manner, it may be conceded that a metal may be considered to be built up of a lattice of metallic ions, the remaining electrons of the individual atoms being considered free or partly bound in accordance with their energy values. The susceptibility of the metal (non-ferromagnetic) is the sum of the susceptibility of the ions and that of the extra-ionic electrons. The well-known theory of Langevin[4] explains in an admirable manner the diamagnetism of inert gas atoms and ions which similarly possess closed electronic configurations. The methods of calculating the mean square radius in the Langevin expression have been greatly extended by Van Vleck,[5] Pauling,[6] Hartree and Stoner,[7] Slater[8] and Angus.[9] The theoretical estimates of the ionic susceptibilities agree remarkably well with the experimental values of Joos and Kido.[10]

The extra-ionic electrons may be considered free or partly bound and their contribution to the metallic susceptibility depends on the nature of their binding.[11] The problem of the paramagnetism of the electrons having a very low energy of binding and hence considered free, has been the subject of extended investigations by Pauli[12] who applied the Fermi-Dirac statistics. Bloch[13] has extended Pauli's relation and obtains for the atomic susceptibility of the free electrons in the metal the relation

$$(\chi_A)_e \times 10^6 = 48{\cdot}17q/V_0\,[1 - 6{\cdot}113 \times 10^{-9}\,(T/V_0)^2],$$

where q is the number of electrons considered as free in the metal per atom,

V_0 the width of the energy band occupied by the electron in volts and T the absolute temperature. Superposed over this we have the Landau[14] diamagnetism which is one-third of the Pauli paramagnetism. Thus in the metallic type of binding, the electrons contribute a paramagnetic component. If on the other hand, the outer electrons are considered as bound, they would offer a diamagnetic contribution, the magnitude of which is considerable when the binding is of the Ehrenfest-Raman type[15] and much less when it is homopolar.

In view of the above conclusions, a study of the magnetic properties of metals and particularly of single crystals is of special interest. A knowledge of the susceptibility variation in different directions in single crystals helps us to infer the nature of binding of the extra-ionic electrons in these directions. The susceptibility component of the ions is constant for a given ion while that of the extra-ionic electrons is dependent on the several physical conditions of the metal under investigation.

One direction in which the susceptibility of the metal has been studied is the change due to cold-working. The effect was first noticed by Seemann and Vogt[16] who found that cold-worked copper, silver, platinum and bismuth had different susceptibilities from the annealed specimens. Honda and Shimizu[17] obtained also similar changes and found that the diamagnetism of copper and silver decreased on cold-working. Bitter[18] noticed considerable departure in the cases of copper and silver but Banta,[19] and later Heaps and Banta,[20] showed that no measurable changes were observable when these metals were subjected to cold-working. Lowance and Constant[21] obtained results similar to those of Honda in the cases of copper, silver and platinum. Bismuth showed a gradual decrease in diamagnetism on stretching.

In later investigations Honda and Shimizu[22] repeated their earlier work in view of the suggestion of Kussmann and Seemann[23] that on cold-working, the ferromagnetic impurities crystallised out and hence caused a decrease in diamagnetism. On correcting for the presence of such impurities at different density values of copper, silver and gold, Honda and Shimizu found an increase in diamagnetism on cold-working. For platinum and aluminium, the paramagnetic susceptibility of the metals decreased on cold-working.

In more recent investigations,[24] they have accounted for these and other similar phenomena (like melting and change of crystal structure) where changes of susceptibility are observed by considering the effect of change of density on the susceptibility of the free electrons. When the density of the metal decreases by cold-working, there is a decrease in the number of free electrons and an increase in the number of bound electrons. The first result gives rise to decreased paramagnetism, while the second is

accompanied by increased diamagnetism. They have deduced expressions for these changes and find that the calculated alterations in susceptibility agree with the experimental results in a number of cases. The interest created by these investigations leads one naturally to a more thorough and systematic study of the changes in susceptibility due to cold-working in the cases of other important metals. Also the effects of stress on single crystals from the point of view of magnetic properties should be of considerable interest and importance. In this part, a careful study is made of the magnetic susceptibilities of a few cold-worked metals prepared in the form of polycrystalline rods. In the next part the results obtained by similar studies on single crystals of a few metals are given.

2. *Experiment.*

(*a*) *Metals.*—The metals investigated here are bismuth, zinc, cadmium and tin. They were extra pure from Kahlbaum. Spectroscopic analysis of the samples showed the presence of negligibly small quantities of impurities.† The specimens were tested for ferromagnetic impurities by investigating the susceptibility values at different field strengths. This point will be described at length later in the paper.

(*b*) *Preparation of polycrystalline rods.*—For the study of the magnetic properties, polycrystalline rods had to be prepared, having lengths between 10 and 15 cm. and diameters between 2 and 5 mm. This was done with the help of the tube shown in Fig. 1. The tube was cleaned thoroughly

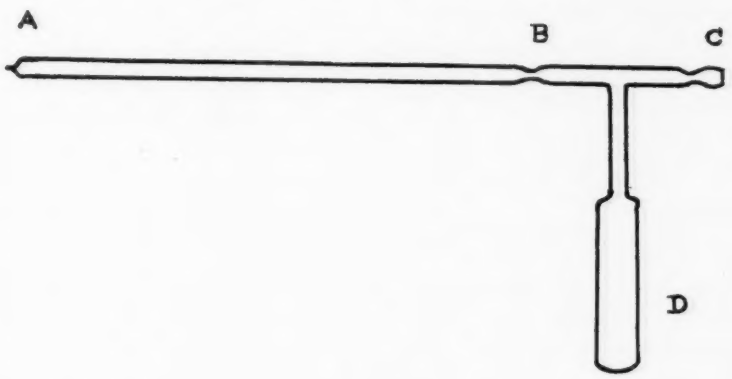

FIG 1.

† The chief impurities were as follows:—(*a*) Bismuth-copper 0.001%, silver 0.01% and lead 0.001%; (*b*) zinc-cadmium 0.001% and lead 0.001%; (*c*) cadmium-zinc 0.01% and lead 0.001%; (*d*) tin-copper 0.001% and lead 0.01%.

and a sufficient quantity of the metal was taken in D. The end C was connected to a pump and the pressure reduced to the lowest possible value. The metal in D was then melted and after shaking several times to remove all absorbed gases, the clean metal was allowed to flow in AB. After cooling, the specimen rod in AB was removed by cracking the glass all around and breaking it.

(*c*) *Measurement of susceptibility.*—The Guoy method was adopted for the measurement of the susceptibility of the metal specimens. The electromagnet was one of the Pye type and the pole faces of 3 cm. diameter were fixed parallel to each other at a distance of $1\frac{1}{2}$ cm. Measurements were made at different field strengths for any given sample by varying the current through the electromagnet from 3 to 7 amperes. The intensities of the magnetic field vary under these circumstances from 7·5 to 17 kilogauss.

The cylindrical rod of metal was suspended by a fine wire from one arm of a chemical balance. The specimen was arranged to have its axis vertical and the lower metal surface to lie symmetrically between the pole faces. The weights of the rods were first determined in the absence of the magnetic field and then successively for different currents through the electromagnet. The weights could be determined correctly to one-tenth of a milligram.

Water was used as the standard substance. A glass tube of uniform diameter and about 25 cm. in length was half-filled with water and measurements were made at different field strengths with the water surface symmetrically between the pole faces.

Let κ_m be the volume susceptibility of the metal specimen, a_m its area of section, H the intensity of the magnetic field between the pole faces, H_m the intensity of the field at the upper end of the rod and mg the force on the specimen due to the field. Then

$$\tfrac{1}{2}\,\kappa_m a_m\,(H-H_m)^2 = mg.^{\ddagger}$$

Similarly for water

$$\tfrac{1}{2}\,\kappa_w a_w\,(H-H_w)^2 = m'g.$$

Hence

$$\kappa_m = \kappa_w \frac{a_w}{a_m} \cdot \frac{(H - H_w)^2}{(H - H_m)^2} \cdot \frac{m}{m'}$$

Or

$$\chi = \frac{\kappa_m}{\rho} = \frac{\kappa_w}{\rho} \cdot \frac{d_w^2}{d_s^2} \cdot \frac{(H - H_w)^2}{(H - H_m)^2} \cdot \frac{m}{m'}$$

‡ In the case of bismuth, the Guoy force being large (about ¼ gr. weight), χ was determined directly by this equation. The intensities of the magnetic field were determined at different currents by the search coil method.

where d_w and d_s are the diameters of the water column and the metal rod and ρ the density of the metal. The specific susceptibility was calculated from the above expression.§

(*d*) *Cold-working.*—The rods were subjected to tensional stress by the application of weights. After the application of the stress, the ends were cleaned in dilute hydrochloric acid and the susceptibility determined once again. The ends of the rod were slightly deformed but since one of them was placed in the uniform field and the other in a field of relatively small intensity, the deformations did not influence the results.

The densities were determined by weighing the samples in air and water. The susceptibilities of the cold-worked metals were then determined by measuring the Guoy forces on each rod at different field strengths.

Test experiments were made by determining the Guoy forces with any one sample inverted and also with the specimen below the pole faces in which case (the metal being diamagnetic), the force will be downward and more weight will have to be added to the other pan for equilibrium. The differences were very small and safely within the errors of measurement. These test experiments are highly important since they show that ferromagnetic impurities occur well distributed in the samples and are not concentrated in certain specific regions.

3. *Results.*

(*a*) *Bismuth.*—The specimens studied had a density of 9·798 gr. per c.c. The diamagnetic susceptibility of the unstrained specimens was found to be 1·412.‖ The rods cast had diameters of 4 mm. and the Guoy force amounted to about quarter of a gram weight at a current of 6 amperes through the electromagnet. Since the measurements were made accurately to one-tenth milligram the susceptibility values may be taken correct to 0·1 per cent. The mean value obtained for the metal agrees satisfactorily with those of other investigators as detailed in Table I.

It will be remembered that Honda and Owen adopted the Curie method and applied careful corrections for the presence of ferromagnetic impurities. Focke obtained 1·340 as the mean value for a polycrystalline aggregate of the metal from his values of the principal susceptibilities observed with single crystals. The earlier value of 1·323 obtained by the author was

§ Actually, however, a correction for the volume susceptibility of air had to be introduced. κ_a be the value for air (0.029×10^{-6} at 30°C.), χ is given by the relation

$$\chi = \frac{\kappa_m}{\rho} = \frac{\kappa_a}{\rho} + \frac{\kappa_w - \kappa_a}{\rho} \cdot \frac{d_w^2}{d_m^2} \cdot \frac{H^2 - H_w^2}{H^2 - H_m^2} \cdot \frac{m}{m'}.$$

‖ All susceptibility values in this paper are given in 10^{-6} units.

TABLE I.

Investigators	Diamagnetic Susceptibility
Honda[1] ..	1·458
Owen[2] ..	1·40
Focke[25] ..	1·340
Rao (1932)[26] ..	1·323
Author ..	1·412

uncorrected for the ferromagnetic impurities. The value obtained in the present investigation agrees with those of Honda and Owen. After cold-working the relative densities of the specimens were determined. The magnetic measurements for each specimen were then made at different field strengths and the susceptibility value at infinite field strengths was obtained by extrapolation from the graph. The specific susceptibilities obtained for different specimens after cold-working are given in the following table. The error in the χ values may be taken to be less than $\frac{1}{2}\%$.

TABLE II.

Relative density of the specimen ρ	$\delta\rho$	Specific diamagnetic susceptibility
9·798	0·000	1·412
9·792	0·006	1·410
9·782	0·016	1·398
9·771	0·027	1·373
9·765	0·033	1·365
9·756	0·042	1·340
9·748	0·050	1·319
9·727	0·071	1·271
9·721	0·077	1·252
9·707	0·091	1·210

A scrutiny of the above table shows that as the density of the metal decreases, the diamagnetic susceptibility also decreases. A graph connecting the values in the second and the third columns is shown in Fig. 2 (*a*). It is found that the curve is almost a straight line.

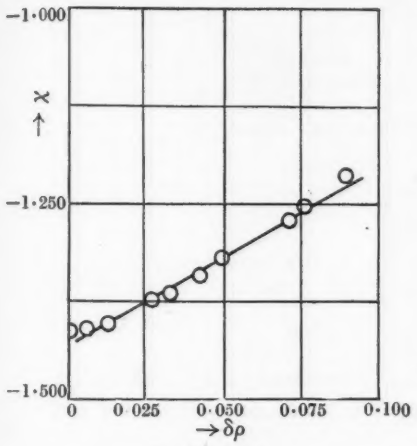

FIG. 2 (*a*)—Bi.

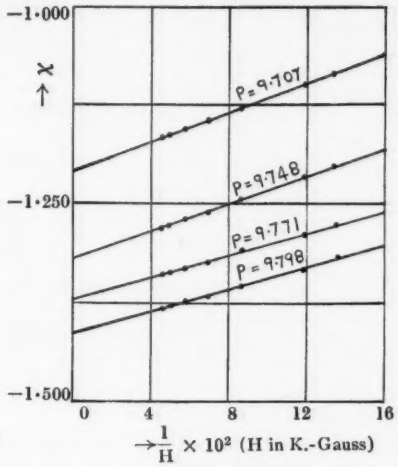

FIG. 3 (*a*)—Bi.

The susceptibilities of an unstrained specimen and of three cold-worked specimens at different field strengths are shown in Fig. 3 (*a*). The graphs connecting the specific diamagnetic susceptibility and the inverse of the field intensity have been produced backwards and the susceptibility at $1/H = 0$ (*i.e.*, at infinite field strengths) has been taken as the value of the specimen concerned. A point of special interest lies in the fact that the tangents of the straight line graphs are not equal. These tangents for the four specimens of densities 9·798, 9·771, 9·748 and 9·707 are found from the graphs to be in the ratio 1 : 1·05 : 1·30 : 1·46. This observation shows that the susceptibility contribution by the ferromagnetic impurities increases as the metal is cold-worked. This important conclusion supports the view put forward by Kussmann and Seemann[23] that on cold-working, ferromagnetic impurities crystallise out and thus cause a decrease in diamagnetism. However, our results show conclusively that such precipitation cannot account completely for the fall of the diamagnetic susceptibility value on cold-working.

(*b*) *Zinc.*—Zinc rods were prepared to have diameters of about 2·5 and 4 mm. The density of the metal was found to be 7·120 and the diamagnetic susceptibility of the unstrained metal was found to be 0·160. The Guoy forces for the two diameters studied were nearly 10 and 25 milligrams at a magnet current of 6 amperes. The mean value of the specific diamagnetic susceptibility for the metal deduced at infinite field strengths and the values obtained by other investigators are given in Table III.

TABLE III.

Investigators	Specific diamagnetic susceptibility
Honda[1] ..	0·154
Owen[2] ..	0·158
Koenigsberger[27] ..	0·130
McLennan, Ruedy and Cohen[28] ..	0·160
Author ..	0·160

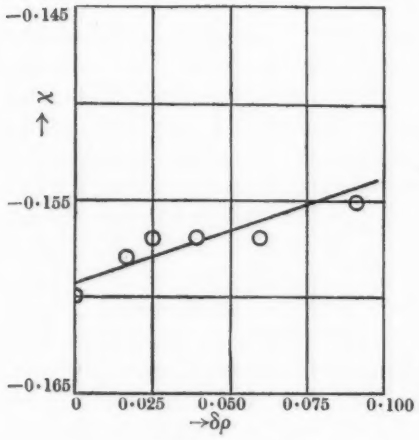

FIG. 2 (*b*)—Zn.

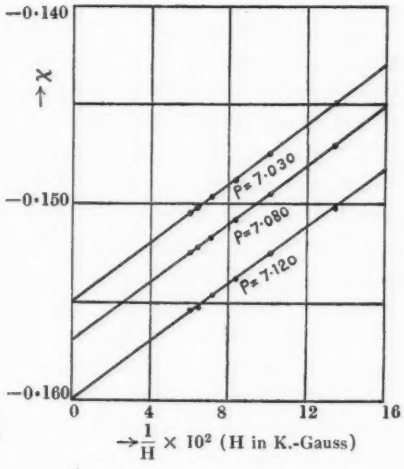

FIG. 3 (*b*)—Zn.

The author's value agrees satisfactorily with those obtained by Honda and Owen and the value deduced from measurements on the principal susceptibilities obtained with single crystals by McLennan, Ruedy and Cohen.

The following table shows the changes of the diamagnetic susceptibility of zinc due to cold-working.

TABLE IV.

Relative density of the specimen ρ	$\delta\rho$	Specific diamagnetic susceptibility
7·120	0·000	0·160
7·103	0·017	0·158
7·095	0·025	0·157
7·080	0·040	0·157
7·061	0·059	0·157
7·030	0·090	0·155

The results are plotted on a graph shown in Fig. 2 (*b*). The decrease in the susceptibility is small when compared with the case of bismuth. The susceptibility of a few specimens at different field strengths are plotted against 1/H in Fig. 3 (*b*). It will be seen that the iron content is small and that the straight lines are almost parallel to each other. The susceptibility values given in the above table have all been obtained by extrapolation to infinite field strengths.

(*c*) *Cadmium.*—Cadmium rods had also diameters of 2·5 or 4 mm. The metal had a density of 8·626 and a diamagnetic susceptibility of 0·174. The Guoy forces at a magnet current of 6 amperes were about 15 and 35 milligrams for the two diameters. The diamagnetic susceptibility values of 0·174 obtained for the metal by extrapolation to infinite field strengths compares favourably with those of other investigators as can be inferred from the following table.

TABLE V.

Investigators	Specific diamagnetic susceptibility
Honda[1] ..	0·169
Owen[2] ..	0·185
McLennan, Ruedy and Cohen[28] ..	0·180
Author ..	0·174

The susceptibilities of the cold-worked specimens are tabulated below.

TABLE VI.

Relative density of the specimen ρ	$\delta\rho$	Specific diamagnetic susceptibility
8·620	0·000	0·174
8·601	0·019	0·174
8·586	0·034	0·173
8·567	0·053	0·173
8·530	0·090	0·172
8·505	0·115	0·170
8·480	0·140	0·169

As in the case of zinc, there is a small yet definite decrease in the susceptibility due to cold-working. The results are plotted in Fig. 2 (*c*). The susceptibilities of a few specimens have also been plotted against 1/H in Fig. 3 (*c*). It will be noticed that the ferromagnetic impurities are small

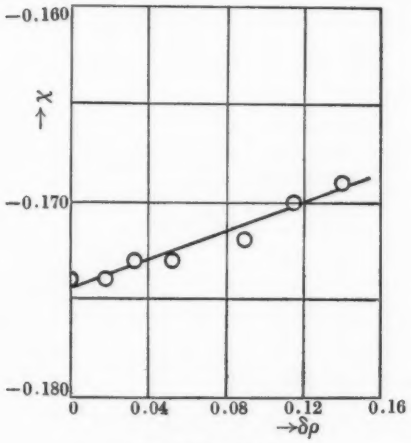

FIG. 2 (*c*)—Cd.

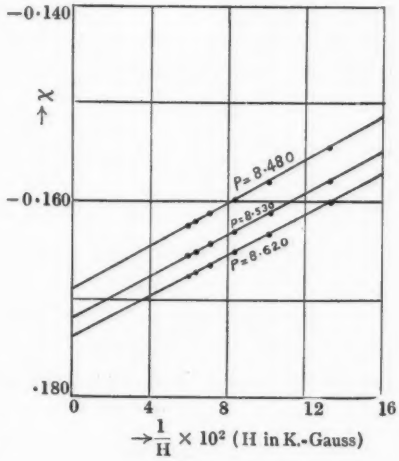

FIG. 3 (*c*)—Cd.

and that no precipitation as suggested by Kussmann and Seemann takes place in this instance.

(*d*) *Tin.*—Tin is of special interest, because of its three allotropic modifications of which white tin and grey tin are the more important. White tin is feebly paramagnetic while grey tin is comparatively strongly diamagnetic. White tin when cooled below 18° C. passes off into the grey variety, the speed of transformation being greatest at about −45° C.[29] The crystal structure of white tin is tetragonal while that of the grey tin is cubic.[30] Honda and Shimizu[31] noticed that the effect of cold-working on white tin was to decrease its paramagnetic susceptibility and in certain cases to make it diamagnetic, thus reversing the sign of the susceptibility. The investigations of the author on tin powder[32] show that fine powders, having diameters below about 1·4μ are diamagnetic, the diamagnetic susceptibility increasing as the particle size decreases. Honda and Shimizu[31] have drawn attention to the similarity of behaviour in the magnetic properties of white tin due to cold-working and to colloidalisation.

The rods of white tin prepared in the present investigation had diameters of 5 mm. The density of the unstrained metal was 7·262 and the paramagnetic susceptibility 0·034. The Guoy force at a magnet current of 6 amperes was found to be nearly 10 milligrams. The following table gives the susceptibility values obtained by different investigators.

TABLE VII.

Investigators	Specific paramagnetic susceptibility
Owen[2] ..	0·02
Honda[1] ..	0·027
Meyer[33] ..	0·038
Wills[34] ..	0·052
Rao (1934)[32] ..	0·036
Rao and Subramaniam[35]	0·038
Hoge[36] ..	0·0259
Author ..	0·034

The value of Hoge given in the above table has been deduced from the principal susceptibilities obtained with single crystals of white tin. The author's value agrees very well with those of other investigators. The following table gives the values of the susceptibility for different cold-worked specimens.

TABLE VIII.

Relative density of the specimen ρ	$\delta\rho$	Specific susceptibility
7·262	0·000	+ 0·034
7·250	0·012	+ 0·025
7·241	0·021	+ 0·012
7·228	0·034	+ 0·002
7·213	0·049	— 0·008
7·191	0·071	— 0·030

A source of some uncertainty in these measurements lies in the fact that on the application of tensional forces, there was a tendency for the metal to narrow down in certain regions. This caused a non-uniformity in the diameter along the length of the rod.¶ Due precautions were however taken to isolate only such lengths as were uniform and appropriate corrections were applied for the field intensity at the other end.

The graph connecting the susceptibility and the change of density of the metal after cold-working is shown in Fig. 2 (*d*). It will be seen that at a density of 7·225 the metal is perfectly non-magnetic. At lower density values, the susceptibility becomes diamagnetic.

In Fig. 3 (*d*) are shown the variations of the susceptibility of a few specimens with 1/H. The ferromagnetic content is very small and the straight lines are almost parallel to each other. The question of the precipitation will, in any case, not account for the decrease in the paramagnetic susceptibility since such an effect will increase the paramagnetism and if

¶ This is obviously due to the fact that the crystals are of larger size in the tin rods than in the case of the other metals.

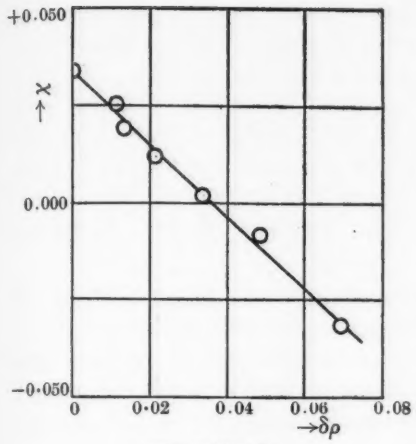

FIG. 2 (*d*)—Sn.

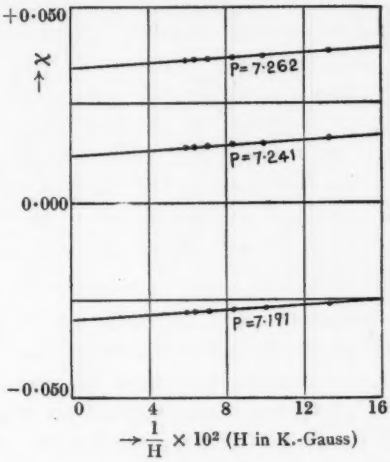

FIG. 3 (*d*)—Sn.

it exists, it will tend in this case to diminish the observed effect due to cold-working.

Experiments showed that on re-melting the cold-worked metals and recasting them into rods, the susceptibilities regained the values for the unstrained metals.

4. *Discussion.*

Our investigations indicate clearly that after the necessary corrections are made for the presence of ferromagnetic impurities, the diamagnetic susceptibility of bismuth is lowered effectively by cold-working. The decrease however is not so striking in the cases of zinc and cadmium. The paramagnetic susceptibility of white tin, on the other hand, decreeases as the density decreases due to cold-working and changes sign at sufficiently low density values. This observation was also made by Honda and Shimizu. We have therefore three different kinds of behaviour because of cold-working.

No consistent explanation has so far been offered to account for the phenomenon accompanying cold-working of metals. The suggestion of Kussmann and Seemann, to which reference has already been made, to the effect that ferromagnetic impurities crystallise out on cold-working, cannot account for the whole of the observed phenomenon. Honda and Shimizu found that in the case of copper and silver, the diamagnetic susceptibility increases on cold-working, after correcting for the ferromagnetic precipitation. A decrease is observed in the case of bismuth.

In all such considerations, due account should be taken of the nature of polycrystalline metals.[37] When metals solidify from the liquid state, the solid is usually composed of aggregates of small crystals. These small crystalline regions do not possess any regular plane boundaries. The size of the individual crystals depends on the rate at which the metal has been cooled from the liquid state. It may be safely assumed that under the conditions outlined in this investigation, these crystals are too small when compared with the dimensions of the metal rods experimented upon. Each individual crystal however retains the properties of the crystalline substance.

There is every reason to believe that there is an amorphous layer of metal in the boundaries between the various crystals.[38] In fact this layer acts as a cement binding loosely the various small crystals together. The very interesting experimental investigations of Beilby throw much light on the existence and function of the amorphous boundary in polycrystalline metals.

Tensile tests on single crystals and polycrystalline material give valuable information regarding the nature of both. For a given stress the extension is generally several times greater for the crystal than for the polycrystalline metal.[39] It is obvious from this result that in the polycrystal a good part of this stress is taken up by the amorphous layer resulting perhaps in the formation of more amorphous matter on the planes of slip. This possibility will also result in the production of greater hardness at larger deforming stresses. Part of this stress is of course utilised in producing deformation in the small crystals constituting the whole metal. The extension of the rod is due to such deformation. Such specific lattice extension accounts for the changes in the character of X-ray reflections observed with cold-worked metal specimens, namely, the elongation of the Laue spots and in the case of monochromatic X-rays, a broadening of the lines of the spectrum.[40] At sufficiently large stresses there is considerable elongation of the crystals in the direction of the stress until in extreme cases, the well-known *faserstruktur* results. The lowering of density observed with cold-worked specimens has been attributed to the formation of amorphous metal on the planes of slip.[38]

These changes occurring inside the polycrystalline matter because of the application of stresses lead us to a natural explanation of the magnetic effects due to cold-working. The boundary area should be fairly large considering the small size of the crystals. The two effects outlined above, namely, the formation of more amorphous matter in the boundary and the

lattice distortion in the small crystals, must together be responsible for the magnetic effects accompanying cold-working.‖

If the binding of the valency electrons is of the Ehrenfest-Raman type, these effects would together contribute to a decrease in the diamagnetic susceptibility. The conversion into amorphous form will result in the disruption of many of the large orbits, and the distortion in the small crystals of these orbits would result in the introduction of a paramagnetic component. These considerations explain the observed effects with bismuth. In the case of homopolar binding, there is not likely to be any change in the susceptibility due to the first effect but the second may introduce a distortion in the orbits of the outermost electrons. This will introduce a small paramagnetic component. Zinc and cadmium seem to come under this class.

The special case of metallic binding is more complicated. This problem has been dealt with at length by Honda and Shimizu. When the density of the metal decreases, there is a decrease in the number of free electrons. The consequent decrease in paramagnetic susceptibility is given by[41]

$$\delta\chi_1 = \tfrac{2}{3}\frac{CL^{1/3}}{W^{1/3}}\left(-\tfrac{2}{3}\rho^{-5/3}\alpha^{1/3}\,\delta\rho + \tfrac{1}{3}\alpha^{-2/3}\rho^{-2/3}\,\delta\alpha\right),$$

where $C = 2{\cdot}21 \times 10^{-14}$, L = Loschmidt number, W = the atomic weight, ρ = density and α = number of free electrons per atom.

Simultaneously we have an increase in the number of bound electrons and the increase in the diamagnetic susceptibility is given by[42]

$$\delta\chi_2 = \frac{3{\cdot}1 \times 1{\cdot}84 \times 10^{-5}}{W} \cdot \tfrac{1}{3}\alpha^{-2/3}\,\delta\alpha$$

‖ Note added in Proof:—

The production of amorphous matter in the boundary, however, does not receive support from more recent X-ray data. But in a modified form, it is possible to enunciate this theory to satisfy all the requirements of experiment. This modified theory postulates some form of breaking up of the crystal structure on slip planes between the small crystals. This may result in an extension of the lattice or in a bending of the planes near the surface or both. Hengstenberg and Mark (*Zeits. f. Phys.*, 1930, **61**, 435) studied the X-ray reflection from cold-worked metals (Mo, W and Ta) and they concluded that at least part of the distortion consists of a random displacement of the atoms from their normal positions. Brindley and Spiers (*Phil. Mag.*, 1935, **20**, 882) have verified the existence of such random displacements in filed powders of copper and nickel. Wood (*Phil. Mag.*, 1934, **18**, 495) studied the broadening of X-ray reflections from cold-worked metals and suggested also that the observed effects may be due to some kind of lattice distortion, either random or regular.

The balance of X-ray evidence may be taken to point out to a random displacement of the surface atoms in the small crystals composing the polycrystals. Such random disturbance would mean lower density since cold-worked metals show smaller density values than the annealed specimens. The boundary of the small crystals have a distorted structure and this may account in a disruption or distortion of the Ehrenfest-Raman orbits which would result in a smaller diamagnetic susceptibility value.

where δa according to Honda, Nishina and Hirone[43] is given by

$$\delta a = \frac{A}{3}\left(\frac{4\pi\rho}{3M}\right)^{0.488}\frac{\delta\rho}{\rho}$$

where $A = 2{\cdot}261 \times 10^{-12}\ Z^{0{\cdot}513}$ and M = mass of the atom.

Honda and Shimizu have successfully applied these postulates to the changes of susceptibility accompanying (*a*) the conversion of white tin into grey tin, (*b*) the melting of white tin, gold, silver and copper, and (*c*) cold-working of silver, copper and platinum. From the structure of polycrystalline metals outlined above, it looks doubtful whether the theory could be applied to the case of cold-working. In fact, in the calculations of Honda and Shimizu, there is better coincidence observed in the cases of melting and allotropic transformation than in the case of cold-working.

In the particular instance of tin, there is little doubt that the change of crystal structure accounts for the change of susceptibility when white tin is converted into the grey variety. When the metallic linkages change over into homopolar bonds, there is a change of susceptibility. Since in homopolar linkages, we have the susceptibility following approximately the principle of additivity, the conversion of white tin into the grey type (in which case we have homopolar binding) or into the amorphous form would result in the same general change in susceptibility. These ideas are supported by the author's work on tin powder,[32] in which it was noted that the extrapolated susceptibility value at extremely small particle sizes almost coincided with the value for grey tin. We have here, therefore, a satisfactory explanation for the changes observed in cold-worked tin.

Further discussion is reserved for Part II, wherein the results obtained with single crystals of a few metals will be reported.

5. *Summary.*

The effect of cold-working on the susceptibilities of bismuth, zinc, cadmium and tin is studied. The diamagnetic susceptibility of bismuth is lowered effectively while zinc and cadmium show a small decrease. The paramagnetic susceptibility of white tin shows a decrease as the density decreases due to cold working and changes sign below a particular density value. The nature of polycrystalline metals is examined and attention is drawn to the existence of a deformed boundary between the small crystals in the metal specimen. Natural explanations are offered for the observed susceptibility changes in the light of the existence of the distorted layer and of the author's work on metallic colloidal powders. The results obtained with single crystals of some metals will be reported in the next part.

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PIGMENTS OF COTTON FLOWERS.

Part III. Karunganni (*Gossypium indicum*).

By K. Neelakantam
and
T. R. Seshadri.
(From the Department of Chemistry, Andhra University, Waltair.)

Received January 29, 1936.

Karunganni (*G. indicum*) is a dry-land cotton widely grown in South India. Its lint is better than that of Uppam (*G. herbaceum*) but the flower petals are similar being golden yellow with crimson spots at the base. For purposes of this investigation they were collected from the Cotton Research Station, Coimbatore.

During the cotton season of 1932 one of us (T. R. S.) made a preliminary examination of the petals using about 200 grams of dried material and found that they contained mainly Quercimeritrin and Gossypitrin. After making the usual extraction with alcohol and removing as much of the solvent as possible, the pigment was taken up with water, precipitated with neutral lead acetate and this portion alone was examined since a subsequent precipitation with basic lead acetate yielded very little more. By repeated crystallisation from alcohol Quercimeritrin and Gossypitrin were separated and identified by means of their colour reactions, the preparation of their acetyl derivatives, hydrolysis to the aglucones and the preparation of the acetyl derivatives of the aglucones.

A larger sample was collected in 1933 and examined in detail according to the method already outlined in the previous papers of this series (Neelakantam, Rao and Seshadri, 1935). The pigments were isolated in five different fractions: (1) sparingly soluble in alcohol and coming out on concentrating the alcoholic extract, (2) sparingly soluble in water and getting deposited from the aqueous solution obtained after removing alcohol, (3) obtained by ether-extracting the aqueous solution, (4) the neutral lead acetate fraction precipitated as the lead salt on the addition of neutral lead acetate to the aqueous solution, and (5) the basic lead acetate fraction. From (1) was readily obtained a golden yellow solid which has been found to be a complex glucoside of Gossypetin melting with decomposition at 230° and has been named 'Gossypin'. It seems to have the formula $C_{28}H_{24}O_{18}$.

Fraction (2) yielded a pale yellow solid, melting at 255–7° with slow decomposition and non-glycosidic in nature. Its formula seems to be $C_{16}H_{12}O_7$. Fraction (3) consisted of Quercetin whereas fraction (4) was found to be composed of Quercetin, Gossypetin, and a new aglucone previously obtained from *Gossypium herbaceum* (Neelakantam, Rao and Seshadri, 1935) and to which we now give the name 'Herbacetin'. The two latter were present mostly as their glucosides Gossypitrin and Herbacitrin which could not be isolated pure but their presence was ascertained from their colour reactions and the detection of glucose as one of their products of hydrolysis. Fraction (5) was very small and was made up of Quercetin only. No Quercimeritrin could be detected in this large sample, though Quercetin was easily isolated; Gossypitrin was present in smaller quantities only, the main bulk of the Gossypetin glucoside being 'Gossypin'.

The details of the constitution of (i) Gossypin, (ii) the new non-glycosidic pigment, and (iii) Herbacitrin are under investigation.

Experimental.

Fraction 1. *Isolation of Gossypin.*—Dried and powdered petals of Karunganni (1400 g.) were repeatedly extracted with rectified spirits and the extract concentrated to about 800 c.c. On allowing to stand for over a week a yellow crystalline solid was deposited. It was filtered and washed with a little alcohol (yield 4 g.). It was very sparingly soluble in alcohol, ether or pyridin and dissolved readily in boiling water to form a yellow solution from which sheaves of golden yellow needles separated out on cooling. Though it was easily soluble in hot acetic acid, this solvent could not be used for crystallisation since the substance came out of it as nodules without any definite crystalline shape. It was purified by twice crystallising from water and twice again from dilute alcohol; the pure substance appeared as glistening golden yellow needles, melting at 230° with decomposition. [Found in air dried sample: C, 46·7, H, 4·5 and loss on drying *in vacuo* at 110°, 10·1%; $C_{28}H_{24}O_{18}$, $4H_2O$ required C, 46·7, H, 4·4 and H_2O (loss), 10·0%. Found in sample dried at 110° *in vacuo*: C, 51·4, H, 3·7; $C_{28}H_{24}O_{18}$ required C, 51·8, H, 3·7%.]

With dilute sodium hydroxide Gossypin gave a deep yellow solution; the colour faded rapidly on shaking with air and soon assumed a faint yellowish brown tinge. Sodium carbonate produced first yellow which changed into greenish yellow and finally pale yellowish brown. On adding cold concentrated hydrochloric acid to the yellow solid it immediately assumed a deep red colour and on heating went into a clear orange red solution which did not deposit anything on cooling. Strong sulphuric acid produced a similar effect and the solution exhibited no fluorescence. Concentrated nitric

acid dissolved the substance readily to give a pale yellow solution. Neutral lead acetate gave a red precipitate and ferric chloride an olive green colour. The substance did not give prominent colour reactions with buffer solutions of different P_H values. At 6·8 a clear yellow solution was produced which was stable for several days. Between 8 and 9·8 the solutions were first yellow and slowly changed to red in about three days whereas at P_H 11·0 the yellow was lost rapidly (15 minutes) and a very pale brown colour resulted. It did not give the Gossypetone reaction in aqueous alkaline solution on shaking with air or in alcoholic solution on treatment with *p*-benzoquinone.

Acetylation of Gossypin with acetic anhydride alone or with sodium acetate was unsuccessful. The substance dissolved and the yellow solution slowly lost its colour on heating. After boiling for 4 hours the acetyl derivative could not be precipitated by adding alcohol as in the case of Gossypitrin. On pouring the acetic anhydride solution into water and allowing it to stand, a colourless amorphous product was obtained and all attempts to obtain it crystalline resulted in failure. When Gossypin was hydrolysed by boiling with 7% sulphuric acid for 2 hours, Gossypetin and glucose were identified as the products. Gossypetin was identified by a comparison of its melting point, colour reactions and melting point of its acetyl derivative with those of the sample obtained from Uppam (*G. herbaceum*). Glucose was identified in the usual way as the osazone.

Fraction 2. *Isolation of a New Pigment.*—The alcoholic mother-liquor left after the removal of Gossypin was further distilled in order to remove as much alcohol as possible, a large volume of water added (1000 c.c.), and the whole heated in a basin on a water-bath in order to remove the remaining alcohol. A large amount of resin separated out. By careful manipulation the hot aqueous solution was decanted and filtered from the resin and concentrated to about 400 c.c. On cooling, no solid separated out. It was therefore extracted with ether repeatedly (4 times with about 100 c.c. each time) and then allowed to stand for a few days. The ether solution was kept separately for examination. The aqueous solution now deposited a pale yellow crystalline solid which was filtered and washed with small quantities of water. It was sparingly soluble in water but easily soluble in aqueous alcohol or pyridin. After two crystallisations from dilute pyridin and two from dilute alcohol it was quite pure and was obtained as pale yellow needles and rhombic plates, melting at 255–7° with slow decomposition. Yield 1·5 grams. [Found in air dried sample: C, 51·8, H, 5·4, loss on drying *in vacuo* at 110°, 14·0%; $C_{16}H_{12}O_7$, $3H_2O$ required C, 51·9, H, 4·9 and H_2O (loss), 14·6%. Found in sample dried *in vacuo* at 110°, C, 60·0, H, 4·4; $C_{16}H_{12}O_7$ required C, 60·7, H, 3·8%.]

The substance was unaffected when boiled for two hours with aqueous or aqueous-alcoholic sulphuric acid and no sugar was produced, and hence it was non-glycosidic. It gave a stable yellow solution with dilute sodium hydroxide or carbonate. Concentrated hydrochloric acid in the cold produced no change whereas on heating a yellow solution was produced. Nitric acid produced a colourless solution. Cold concentrated sulphuric acid gave a yellow solution with a characteristic green fluorescence which became more prominent on diluting with more acid. On pouring this into water, however, a colourless solution resulted. It did not give any noteworthy colour changes with alkaline buffer solutions. Below P_H 10·0 it dissolved only slowly; at P_H 11·0 it gave a permanent yellow solution. Neutral lead acetate produced no precipitate whereas basic lead acetate gave a yellow solid. A drop of ferric chloride, added to an aqueous solution of the substance, produced a yellowish green colour. It was readily acetylated with acetic anhydride and sodium acetate. The acetyl derivative was easily soluble in alcohol and was obtained as colourless needles, melting at 186–7°.

Fraction 3. *Quercetin.*—The ether extract on evaporation gave a brown solid, which after two crystallisations from aqueous pyridin, formed yellow needles (yield 0·5 g.) melting at about 310° with decomposition. Its colour reactions were identical with those of Quercetin and it formed an acetyl derivative melting at 194–5° which was not depressed by admixture with penta-acetyl Quercetin obtained from the Cambodia flowers (*G. hirsutum*).

Fraction 4. *Neutral Lead Acetate Fraction.*—The original aqueous solution left after the separation of Fractions 2 and 3 was treated with excess of neutral lead acetate. The orange red precipitate produced was filtered, washed with water, suspended in water and decomposed with hydrogen sulphide. By concentrating the aqueous solution thus obtained, the pigment was isolated in three fractions and each examined separately. The first two fractions were more easily purified and, after three crystallisations from dilute pyridin, yielded the same crystalline solid melting with decomposition at about 310° and yielding an acetyl derivative melting at 194–5°. It was identified as Quercetin (yield 1·5 g.).

The third fraction could not be crystallised and obtained pure. The colour reactions were very similar to those of Gossypitrin. The sample was hydrolysed with sulphuric acid and the product was crystallised once from dilute acetic acid and a second time from dilute alcohol. Though it now looked quite clean and yellow (yield 1·5 g.) it was still impure, had no definite melting point (260–90°) and could not be purified by further crystallisation. The colour reactions were those of Gossypetin. It was, therefore, acetylated and the acetyl derivative crystallised from a mixture

of acetic anhydride and alcohol. The sparingly soluble fraction which formed the major portion melted at 226–8° and was found to be identical with hexa-acetyl Gossypetin by a mixed melting-point determination. The more soluble fraction (a small yield), which was obtained by pouring the acetic anhydride-alcohol mother-liquor into water, was best crystallised from rectified spirits. It melted at 192–3° and was found to be identical with the acetyl derivative of Herbacetin, the new aglucone which was obtained as its glucoside from Uppam (*G. herbaceum*). The aqueous solution left after the hydrolysis was examined for the presence of sugars, and glucose was identified as the osazone. This was obviously a product of hydrolysis since the original substance in aqueous solution before hydrolysis gave no test for the sugar. It could therefore be concluded that the two aglucones existed mostly as glucosides in the third fraction of the neutral lead acetate precipitate.

Fraction 5. *Basic Lead Acetate Fraction. Quercetin.*—After removal of the neutral lead acetate precipitate the aqueous mother-liquor was treated with excess of basic lead acetate. The yellow precipitate was filtered, decomposed as usual with hydrogen sulphide and the resulting aqueous solution concentrated over a water-bath first and finally in a desiccator. The product was very impure being mixed with a good deal of resinous matter. After two crystallisations from water and two more from dilute pyridin it still remained impure (0·2 g.). The colour reactions were similar to those of Quercetin. On acetylation it gave an acetyl derivative which crystallised from alcohol as colourless needles, melting at 194–5° and which was found to be identical with penta-acetyl Quercetin.

Summary.

A preliminary examination, using a small sample of the flower petals of the Karunganni (*G. indicum*) collected in 1932, showed that the pigments consisted mainly of Quercimeritrin and Gossypitrin. From a study of a larger sample collected in 1933 it was found that the following were the main components : Gossypin, a complex glucoside of Gossypetin ; Quercetin, a new non-glycosidic pigment having the probable formula $C_{16}H_{12}O_7$ and Gossypetin mostly as its glucoside Gossypitrin. A small quantity of Herbacetin, mostly as its glucoside Herbacitrin, first isolated from Uppam (*G. herbaceum*) as a new member of the flavonol series was also found to be present.

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ULTRASONIC VELOCITIES IN ORGANIC LIQUIDS.

Part V. Some Related Groups.

By S. Parthasarathy.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received June 19, 1936.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

Further work on the determination of ultrasonic velocities in organic liquids has been carried out, with a view to elucidating the relationship between chemical constitution and sound velocity. The present paper includes the results on methyl cyclohexanols, methyl cyclohexanones, tertiary amyl alcohol and octyl alcohol (sec.), some related aromatic hydrocarbons and a few compounds containing nitrogen.

The purest available liquids were employed after distillation.

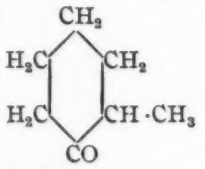
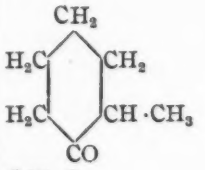
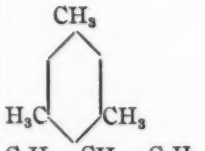
The frequency of vibration was measured for each liquid very accurately by a precision wave-meter and was about $7{\cdot}32 \times 10^6$ c./s. in all cases. The temperatures at which the measurements were made are noted against each liquid.

2. Results.

The following table gives the results of measurements of ultrasonic velocities in a few related groups of organic liquids. The last column contains the values of adiabatic compressibilities calculated from the velocity and density. So far, no determinations appear to have been made either of sound velocity or of adiabatic compressibility for any of these compounds. They are thus made here for the first time.

TABLE.

Ultrasonic Velocities in Related Organic Compounds (Frequency about $7 \cdot 32 \times 10^6$ *c./s.)*

	Liquids	Chemical Formula	Temp. in °C.	Density	Velocity of sound in meters per second	Adiabatic compressibility $\beta_{ad} \times 10^{12}$
1	Methyl cyclohexanol–*o*		25°·5	0·922	1421	53·7
2	Methyl cyclohexanol–*m*	$C_7H_{14}O$	25°·5	0·914	1406	55·3
3	Methyl cyclohexanol–*p*	,,	25°·5	0·920	1387	56·6
4	Methyl cyclohexanone-*o*		25°·5	0·924	1353	59·1
5	Methyl cyclohexanone–*p*	$C_7H_{12}O$	25°·5	0·913	1348	60·3
6	Tertiary amyl alcohol ..	$(CH_3)_2 \cdot C(OH) \cdot C_2H_5$	28°	0·809	1204	117·3
7	Octyl alcohol (sec.) ..	$CH_3 \cdot CHOH \cdot (CH_2)_5 \cdot CH_3$	26°	0·818	1302	72·1
8	Mesitylene ..		28°	0·862	1320	66·6
9	Diphenyl methane ..	$C_6H_5-CH_2-C_6H_5$	28°	1·006	1501	35·1
10	Dekahydronaphthalene (*cis*)	$C_{10}H_{18}$	27°	0·875	1375	60·4
11	Cymene (*para*) ..	$C_6H_4(CH_3)$ $[CH(CH_3)_2]$	28°	0·857	1308	68·2
12	β-Picoline ..	$CH_3 \cdot C_5H_4N$	28°	0·952	1419	52·2
13	Acetonitrile ..	$CH_3 \cdot CN$	28°	0·775	1275	79·4
14	Phenyl mustard oil ..	$C_6H_5 \cdot N : CS$	27°	1·131	1412	44·4

3. Discussion.

As no data are available of previous measurements made on these compounds, we shall only discuss the relationship between the chemical constitution and acoustic velocity.

Methyl cyclohexanols (*ortho, meta and para*).—The velocity for cyclohexanol was determined previously and given in Part I as 1622 m./s. at 23° C. The range of velocities for the three methyl cyclohexanols is from 1387 to 1421 m./s. at 25°·5 C. The sound velocity in the former compound is decidedly higher than that for any of the latter compounds. The introduction of a methyl group, therefore, lowers the acoustic velocity.

o-Methyl cyclohexanol.—This compound has definitely a higher velocity than either for the meta- or para- compound. A good number of such examples, where the ortho-compound showed higher velocity, have been given in earlier parts.

Methyl cyclohexanones (*ortho and para*).—These two compounds have velocities 1353 and 1348 m./s. at 25°·5 C. while cyclohexanone, as given in Part I, possesses 1441 m./s. at 23°·5 C. The velocity in the latter compound is definitely higher. A methyl group in a ketone also lowers the velocity just as much as it does in an alcohol of the cyclohexane family.

o-Methyl cyclohexanone.—This compound has a slightly higher velocity than the para-compound. Such cases of enhanced velocities for the ortho-compounds have been cited before.

Methyl cyclohexanols and methyl cyclohexanones.—In the two sets of liquids investigated above, *i.e.*, alcohols and ketones, the alcohols always show higher acoustic velocity than the ketones. This seems to be the rule almost everywhere. In the compounds, cyclohexanol and cyclohexanone, the former has higher velocity.

Tertiary amyl alcohol.—Amyl alcohol (*n*) has a velocity of 1347 m./s. at 24° C., while the tertiary amyl alcohol has only 1204 m./s. at 28° C. We have remarked elsewhere in other papers that an *iso*-compound has a lower velocity. It does indeed matter, therefore, whether the alcohol is a normal one, a secondary or a tertiary. The normal alcohol shows the highest velocity in that series.

Octyl alcohol (*sec.*).—Even normal amyl alcohol shows as high a velocity of 1347 m./s at 24° C. whereas (*sec.*) octyl alcohol has only 1302 m./s. at 26°C. Thus, in spite of the lengthening of the chain, the effect due to the secondary nature of the alcohol preponderates. This supports the view expressed in the earlier paragraph.

Mesitylene.—We observed in earlier papers that the velocity increases in the series benzene, toluene and xylenes. Now the velocity has been determined in mesitylene, which is trimethyl benzene, and it is found to be 1320 m./s. at 28° C. For the same temperature the ultrasonic velocities in the former group of compounds are much below 1300 m./s. In this series mesitylene shows the highest velocity.

Diphenyl methane.—Two benzene nuclei joined together through a carbon atom has apparently increased the acoustic velocity. The velocity in this compound is higher than that for benzene, and evidently a greater number of benzene rings in a molecule enhances the velocity.

Dekahydronaphthalene.—This is a saturated naphthalene compound having two benzene nuclei condensed together, instead of being joined as in diphenyl methane. The density is comparable to that of mesitylene, but the velocity has increased considerably. It is pointed out that just as complete hydrogenation of benzene brings down the velocity, as in cyclohexane, the velocity for which comes midway between those of benzene and a compound of the aliphatic class, complete hydrogenation of naphthalene should be considered here to have brought down the velocity. For we know that α-mono-chlornaphthalene (Part IV) shows 1462 m./s. at 27° C. in spite of a heavy chlorine atom in it. In properties, dekahydronaphthalene is nearer to an aliphatic than to an aromatic, which explains a rather not high velocity for this compound.

Cymene (*para*).—This has a velocity of 1308 m./s. at 28° C. The densities of *p*-cymene and of mesitylene are comparable and even their velocities as well. The sound velocity for this compound is comparable to a liquid of the unsaturated aromatic class.

β-Picoline.—The velocity for this compound is less than that for α-picoline. Here, if we are permitted to compare the α and β positions as corresponding to the *ortho* and *meta* positions, it is easily understandable as to why the velocity in the α-substituted product should be slightly greater. These cases are analogous.

Acetonitrile.—The velocity in this compound is 1275 m./s. at 28° C. This appears rather high for a liquid of the aliphtic group.

Phenyl mustard oil.—The method adopted here gives an acoustic velocity of 1412 m./s. at 27° C. comparable to those of the aromatic class.

The author records his sincere thanks to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his interest in the work.

Summary.

The paper gives ultrasonic velocities and adiabatic compressibilities in the following compounds: methyl cyclohexanols (*o*, *m*, *p*), methyl cyclohexanones (*o*, *p*), tertiary amyl alcohol, (sec.) octyl alcohol, mesitylene, diphenyl methane, dekahydronaphthalene, *p*-cymene, β-picoline, acetonitrile and phenyl mustard oil. The relation between sound velocities and chemical constitution is discussed.

STUDIES ON THE ANISOTROPY OF THE OPTICAL POLARISATION FIELD IN LIQUIDS—PART IV.

By B. Sundara Rama Rao.
(From the Department of Physics, Andhra University, Waltair.)

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1. Introduction.

In Part III of this series (Sundara Rama Rao, 1936) the variation with temperature of the molar refractivities of some typical associated liquids has been studied. In this paper, it is proposed to examine a pair of isomers, *viz.*, normal butyl alcohol ($C_4H_{10}O$) and ether ($C_4H_{10}O$) and also three members of a homologous series, *viz.*, pentane, hexane and heptane. The choice has again been limited to such liquids for which reliable density data are available. The purpose of the present investigation is to demonstrate the relationship, if any, that might exist between the deviations from Lorentz law and the anisotropy of the molecule. It may be stated even here that with increasing asymmetry in the shape of the molecule we may expect deviations from Lorentz law to become more conspicuous. It is for this reason that pentane, hexane and heptane which constitute a typical set of molecules possessing a progressively increasing geometrical anisotropy are chosen. The liquids have been purified by distillation at constant boiling point before use. A Pulfrich refractometer is used for measuring the refractive indices. The experimental details are the same as those described in Part III.

2. Results.

Table IV is reproduced here from Part I of this series merely for the sake of completeness. Tables I, II, III and V contain the refractive indices.

Table I.

Molar Refractivity of n-*Butyl Alcohol.*

Temp.	10	15	20	25	30	35	40	45	50
Ref. Index ..	1·40226	1·40088	1.39951	1·39804	1·39491	1·39287	1·39083	1·38871	1·38659
Density ..	0·81688	0·81334	0·80979	0·80622	0·80264	0·79904	0·79543	0·79179	0·78815
Mol. Refractivity ..	22·100	22·129	22·159	22·185	22·129	22·126	22·126	22·119	22·114

TABLE II.

Molar Refractivity of Ethyl Ether.

Temp.	10	15	20	25	30
Ref. Index	1·35842	1·35576	1·35278	1·35013	1·34697
Density	0·72503	0·71930	0·71352	0·70767	0·70176
Mol. Refractivity	22·467	22·495	22·506	22·539	22·543

TABLE III.

Molar Refractivity of n-*Pentane.*

Temp.	15	20	25	30
Ref. Index	1·35896	1·35602	1·35313	1·35019
Density	0·63113	0·62629	0·62139	0·61645
Mol. Refractivity	25·154	25·162	25·175	25·186

obtained in the present investigation at different temperatures for *n*-butyl alcohol, ethyl ether, *n*-pentane and *n*-heptane respectively. The densities given in these tables are taken from *I. C. T.* and the molar refractivities are calculated therefrom at all the temperatures at which the refractive indices have been measured.

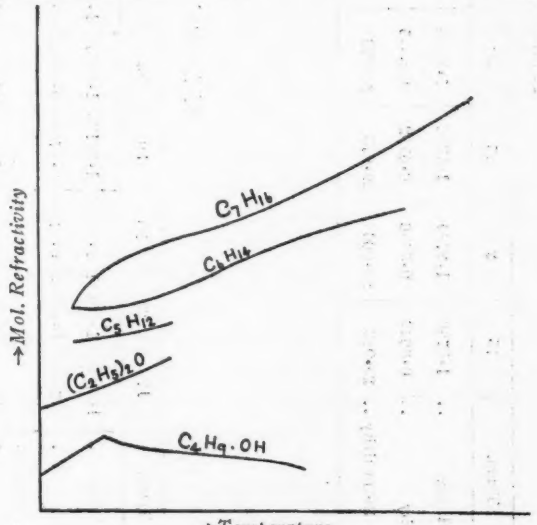

FIG 1.

TABLE IV.

Molar Refractivity of n-*Hexane.*

Temp.	15	20	25	30	35	40	45	50	55	60	65
Ref. Index ..	1·3790	1·3760	1·3732	1·3705	1·3680	1.3652	1·3625	1·3595	1·3568	1·3540	1·3510
Density ..	0·6643	0·6596	0·6552	0·6505	0·6459	0·6412	0·6365	0·6318	0·6270	0·6221	0·6172
Mol. Refractivity ..	29·965	29·966	29·975	29·988	30·019	30·032	30·054	30·052	30·078	30·100	30·108

TABLE V.

Molar Refractivity of n-*Heptane.*

Temp.	15	20	25	30	35	40	45	50	55	60	65	70	75	80
Ref. Index ..	1·39843	1·39641	1·39403	1·39132	1·38871	1·38592	1·38363	1·38106	1·37897	1·37727	1·37427	1·37176	1·36917	1·36662
Density ..	0·68779	0·68356	0·67933	0·67509	0·67082	0·66656	0·66224	0·65795	0·65356	0·64923	0·64474	0·64036	0·63576	0 63133
Mol. Refractivity ..	35·18	35·24	35·27	35·28	35·29	35·29	35·33	35·35	35·41	35·51	35·50	35·53	35·56	35·59

3. *Some Remarks.*

From the curves drawn in Fig. 1,* it may be noticed that the molar refractivity increases with temperature in the series pentane, hexane and heptane. As has already been explained, this may be regarded as normal and it implies that the ratio of the anisotropic coefficients is approaching unity, each of the coefficients tending to become equal to $\frac{4\pi}{3}$. At some stage, which may be different for the different liquids, each of the two coefficients will be equal to $\frac{4\pi}{3}$ and the polarisation field is then of the Lorentz type. At this stage the molar refractivity will be a maximum and thereafter it may be expected to remain constant. It is not however possible to reach this stage by refraction measurements as it is likely to be above the normal boiling point in all these cases. But the interesting point revealed in the present investigation regarding the deviation exhibited by each one of the liquids, say, at the room temperature when we compare the observed molar refractivity at that temperature with the limiting or stationary value may be noted here. In all these cases, the boiling point has nearly been reached and from the calculations given in the following sections it will be noticed that this corresponds roughly to a stage at which p_2/p_1 is about 1·5. In this range, the increase in molar refractivity in heptane is much larger than that in hexane which, in its turn, is larger than that found in pentane. This means that at lower temperatures, say 20° C., the optical polarisation field deviates from the normal Lorentz type considerably in heptane, to a lesser extent in hexane and to a still lesser extent in pentane. These statements are also quantitatively borne out by the figures given in Tables VIII, IX and X.

Similar facts are revealed on comparing the curve for ether with that obtained for butyl alcohol. There is a considerable increase in the molar refractivity of ether, showing that the optical polarisation field is relatively more anisotropic in this case than in its isomer. Ether is, in fact, known to be optically more anisotropic ($r_{vap.} = 0.0256$) than butyl alcohol ($r_{vap.} = 0.0162$) and the figures in Tables VI and VII show the same to be true regarding the geometrical asymmetry also.

The curve for *n*-butyl alcohol is similar to that obtained with associated liquids. The molar refractivity at first increases and then decreases, the observed changes being relatively small.

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* As on previous occasions, the curves indicate only the changes in molar refractivity for each one of the liquids separately. The curves have no significance in relation to the relative magnitudes of the refraction of different liquids.

4. Significance of the Results to the Subject of Light-Scattering.

With the exception of ether for which a reliable value of the refractive index of the vapour is available, the coefficients of anisotropy of the optical polarisation field are calculated in the following by the method indicated in Part III. For ether, the method of Part II is followed. The results so obtained are given in Tables VI to X. Values of r_v, r_l, etc., are taken from Landolt-Börnstein Tabellen.

TABLE VI.

n-*Butyl Alcohol.*

$\delta_v \times 10^3 = 13{\cdot}76$; $\delta_l \times 10^3 = 2{\cdot}30$ $\quad A = 10{\cdot}924 \times 10^{-24}$; $C = 7{\cdot}809 \times 10^{-24}$

Temp.	10	15	20	25	30	35	40	45	50
n_l ..	1·40226	1·40088	1·39951	1·39804	1·39491	1·39287	1·39083	1·38871	1·38659
ρ_1 ..	1·856	2·045	2·405	2·392	2·010	1·988	1·959	1·911	1·862
ρ_2 ..	5·355	5·261	5·081	5·087	5·278	5·289	5·304	5·328	5·352
ρ_2/ρ_1 ..	2·885	2·573	2·113	2·127	2·626	2·660	2·708	2·788	2·874

TABLE VII.

Ethyl ether.

$C = 7{\cdot}737 \times 10^{-24}$; $A = 11{\cdot}775 \times 10^{-24}$ $\quad (n_v - 1) \times 10^6 = 1544$; $r_v = 0{\cdot}0256$

Temp.	10	15	20	25	30
n_l	1·35842	1·35576	1·35278	1·35013	1·34697
ρ_1	0·895	1·029	1·065	1·236	1·228
ρ_2	5·836	5·769	5·751	5·665	5·669
ρ_2/ρ_1	6·521	5·601	5·400	4·583	4·616

TABLE VIII.

n-*Pentane.*

$\delta_v \times 10^3 = 11{\cdot}00$; $\delta_l \times 10^3 = 5{\cdot}49$ $\quad A = 12{\cdot}315 \times 10^{-24}$; $C = 8{\cdot}825 \times 10^{-24}$

Temp.	15	20	25	30
n_l	1·35896	1·35602	1·35313	1·35019
ρ_1	2·908	2·946	3·029	3·083
ρ_2	4·829	4·810	4·769	4·742
ρ_2/ρ_1	1·661	1·633	1·574	1·538

TABLE IX.

n-*Hexane.**

$C = 10{\cdot}605 \times 10^{-24}$; $A = 14{\cdot}650 \times 10^{-24}$ $(n_v - 1) \times 10^6 = 2032$; $r_v = 0{\cdot}015$

Temp.	15	20	25	30	35	40	45	50	55	60	65
n_l ..	1·3790	1·3760	1·3732	1·3705	1·3680	1·3652	1·3625	1·3595	1·3568	1·3540	1·3510
p_1 ..	2·195	2·192	2·180	2·284	2·433	2·507	2·606	2·578	2·717	2·833	2·865
p_2 ..	5·186	5·187	5·193	5·141	5·067	5·030	4·980	4·994	4·925	4·867	4·851
p_2/p_1 ..	2·363	2·366	2·382	2·251	2·083	2·006	1·911	1·937	1·813	1·718	1·693

* This Table differes from Table III of Part II only in having $r_v = 0{\cdot}015$† instead of 0·0115. The values of p_1 and p_2 are recalculated on this basis. † (Landolt-Börnstein Tabellen.)

TABLE X.

n-*Heptane.*

$\delta_v \times 10^3 = 11{\cdot}86$; $\delta_l \times 10^3 = 2{\cdot}102$ $A = 17{\cdot}132 \times 10^{-24}$; $C = 12{\cdot}532 \times 10^{-24}$

Temp.	15	20	25	30	35	40	45	50	55	60	65	70	75	80
n_l ..	1·39843	1·39641	1·39403	1·39132	1·38871	1·38592	1·38363	1·38106	1·37897	1·37727	1·37427	1·37176	1·36917	1·36662
p_1 ..	1·815	2·120	2·239	2·256	2·302	2·293	2·472	2·545	2·843	3·273	3·228	3·378	3·515	3·657
p_2 ..	5·376	5·223	5·164	5·155	5·132	5·137	5·047	5·010	4·862	4·647	4·669	4·094	4·526	4·455
p_2/p_1 ..	2·962	2·464	2·306	2·285	2·229	2·240	2·042	1·969	1·710	1·446	1·420	1·356	1·288	1·218

5. *Discussion of Results.*

Comparison with Earlier Work of Krishnan and Ramachandra Rao.—In an earlier paper Krishnan and Ramachandra Rao (1929) have given a method of calculating the anisotropic coefficients p_1 and p_2 and their variation with temperature from a knowledge of the depolarisation factors at different temperatures. They have studied the cases of pentane, hexane and heptane in detail and have shown that the ratio p_2/p_1 approaches unity with rise of temperature. Their figures also show that at any given temperature, the ratio p_2/p_1 is greatest for heptane and least for pentane. It must be remarked that although in both these respects the conclusions of the present investigation are in entire agreement with those of Krishnan and Ramachandra Rao, there are certain essential respects in which they differ. For example, the fall in p_2/p_1 with rise of temperature is more marked as may be seen from Tables VIII to X than has been indicated by Krishnan and Ramachandra Rao. This is particularly noticeable in heptane in which, according to the author's results, p_2/p_1 changes from 2·5 at 20° C. to 1·2 at 80° C. whereas according to Krishnan and Ramachandra Rao it keeps steady at 2·4 in this range. It may be noted here that while the author's conclusions are based on the measurements of the variation of refractive index in the liquid with temperature, those of Krishnan and Ramachandra Rao are based on the measurements of the variation of the depolarisation factor in the liquid with temperature. It is the experience of the author that the experimental results obtained in the former case, especially with a good refractometer and proper temperature control are usually much more reliable than those obtained in the latter. The actual significance of the observed variations in p_2/p_1 in all the compounds so far studied will be dealt with in a following part.

6. *Summary.*

The molar refractivity is measured at different temperatures for two isomers (*n*-butyl alcohol and ethyl ether) and three consecutive members (pentane, hexane and heptane) of a homologous series. In all these cases, except butyl alcohol, the molar refractivity is found to increase with temperature thus showing that the optical polarisation field is not of the Lorentz type but should be regarded as anisotropic. In butyl alcohol, the molar refractivity at first slightly increases and then diminishes. In these respects it resembles an associated liquid.

In the series pentane, hexane and heptane, the ratio of the coefficients p_2 and p_1 which constitutes a measure of the anisotropy of the optical polarisation field is found to increase as we go up the series and the deviations

from Lorentz law are also more marked in heptane than in hexane and pentane.

With rise of temperature p_2/p_1 rapidly approaches unity in all these cases except butyl alcohol.

The author is highly thankful to Mr. S. Bhagavantam for his helpful guidance in the work.

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1. K. S. Krishnan and S. Ramachandra Rao, *Ind. Jour. Phys.*, 1929, **4**, 39.
2. B. Sundara Rama Rao, *Proc. Ind. Acad. Sci.*, 1936, **3**, 369.

STUDIES ON THE ANISOTROPY OF THE OPTICAL POLARISATION FIELD IN LIQUIDS.—PART V.

By B. Sundara Rama Rao.

(*From the Department of Physics, Andhra University, Waltair.*)

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1. *Introduction.*

From observations on the depolarisation of scattered light at different temperatures, Krishnan and Ramachandra Rao (1929) have calculated the coefficients of anisotropy of the optical polarisation field in liquids and their dependence on temperature. In Part II of this series, the author has derived these constants, making use of the measurements of refractive indices at different temperatures instead of the depolarisation measurements. In the nature of things, the refractive index measurements are bound to be more reliable than those of depolarisation and hence it may be expected that the figures given in Parts I to V of this series give a better indication of the actual state of affairs regarding the dependence of the anisotropic coefficients on temperature than those given by Krishnan and Ramachandra Rao. Hence the values of p_2/p_1 obtained in the present investigation in the case of 8 different liquids at different temperatures are collected here for purposes of convenient comparison. The values given in Table I are corrected to the second decimal place. That the figures are significant only to the first decimal place has already been pointed out. The curves drawn in Fig. 1 graphically represent the trend of variation in the whole list of liquids.

2. *Some Remarks.*

The group of curves drawn in Fig. 1 fall into three distinct classes, *viz.*, the first group consisting of CS_2, C_6H_6, $C_6H_5NO_2$; the second consisting of C_5H_{12}, C_6H_{14}, C_7H_{16} and the third which include CH_3COOH and C_4H_9OH. It will be noticed from these curves that the first class represents liquids in which the fall in anisotropy of the optical polarisation field is *slow* and *regular*. In the second class of liquids the fall is *rapid* and relatively *large in magnitude*. In the third class it is *abnormal* and *erratic*. In the case of acetic acid, the anisotropy increases with increasing temperature whereas

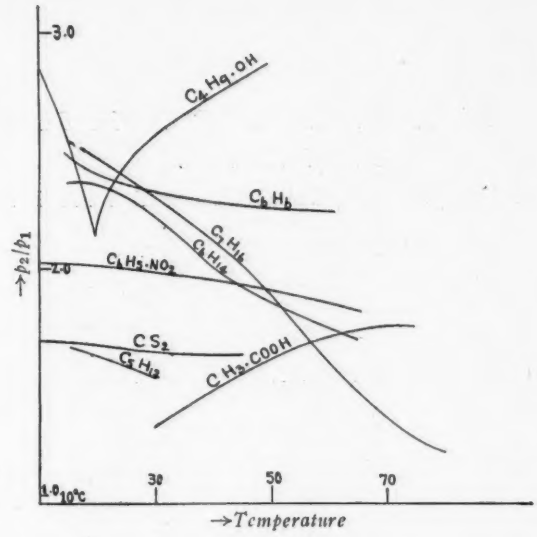

FIG. I.

TABLE I.

Anisotropy of Optical Polarisation Field in Liquids.

Temp. °C.	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80
Carbon disulphide ..	1·69	1·69	1·67	1·65	1·65	1·64	1·64	1·64	..	..	..	..	..	..	..
Benzene	..	2·47	2·41	2·34	2·33	2·31	2·31	2·29	2·26	2·25	2·24	..	..	..	..
Nitrobenzene	2·02	2·01	1·98	2·00	1·98	1·96	1·99	1·93	1·91	1·88	1·86	1·84	..	..	..
Pentane	..	1·66	1·63	1·57	1·54	..	..	..	..	..	..	..	..	..	..
Hexane	..	2·36	2·37	2·38	2·25	2·08	2·01	1·91	1·94	1·81	1·72	1·69	..	..	..
Heptane	..	2·96	2·46	2·31	2·29	2·23	2·24	2·04	1·97	1·71	1·45	1·42	1·36	1·29	1·22
Acetic acid	..	..	..	..	1·32	1·40	1·49	1·57	1·62	1·64	1·71	1·74	1·75	1·76	..
Butyl alcohol	2·89	2·57	2·11	2·13	2·63	2·66	2·71	2·79	2·87	..	..	..	..	..	..

in butyl alcohol it at first diminishes and then begins to increase. This erratic behaviour appears to be connected with the associating nature of the liquids.

REFERENCE.

1. Krishnan, K. S., and Ramachandra Rao, S., *Ind. Jour. Phys.*, 1929, **4**, 39.

THE RAMAN SPECTRA OF SOME BORON COMPOUNDS.

(Methyl Borate, Ethyl Borate, Boron Tri-Bromide and Boric Acid.)

By R. Ananthakrishnan.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

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1. Introduction.

In a paper recently communicated to these *Proceedings*, the author has reported the Raman spectra of propylene and iso-butane and has pointed out certain striking features regarding the state of polarisation of the Raman lines of these substances. It appeared to be of interest to extend the investigation to a few simple compounds of boron, particularly because of the inadequate attention which these compounds have received at the hands of previous investigators. The results of this study are set forth in the present paper.

2. Experimental.

All the chemicals were Kahlbaum's pure reagents. 50 grams of methyl borate, 10 grams of ethyl borate and 10 grams of boron tri-bromide were available in sealed tubes, and were distilled in vacuum before use. Boric acid was in the form of fused sticks, and a saturated aqueous solution at 90° C. was employed in the experiment. The spectra were taken in the usual manner employing a Fuess spectrograph. The plates were measured on a Hilger micrometer with iron arc comparison.

3. Results.

The notations employed in the tables below have the following significance :—

P = Polarised ($\rho \ll \frac{6}{7}$) D = Depolarised ($\rho \backsimeq \frac{6}{7}$)
b = broad *d* = diffuse

TABLE I.

Raman Spectrum of Methyl Borate: $B(OCH_3)_3$.

No.	ν	Assignment	Int.	ρ	No.	ν	Assignment	Int.	ρ
1	19948	$e-2990$	$\frac{1}{2}bd$	D	21	22412	$e-526$	2	D
2	19961	$e-2977$	2	P	22	22620	$e-318$	5	P
3	19945	$e-2943$	4	P	23	22742	$e-196$	$6b$	D
4	20022	$e-2916$	$\frac{1}{2}$	P	24	23136	$e-198$	$3b$	D
5	20068	$e-2870$	4	P	25	23245	$k-1460$	$6b$	D
6	20100	$e-2838$	$\frac{1}{2}$	P	26	23260	$e-322$	1	P
7	21478	$e-1460$	$6b$	D	27	23489	$i-1027$	$\frac{1}{2}$	D
8	21533	$i-2983$	$\frac{1}{2}b$	D	28	23531	$k-1174$	$1b$	D
9	21573	$i-2943$	1	P	29	23588	$k-1117$	1	P
10	21604	$i-2912$	0	P	30	23674	$k-1031$	6	D
11	21649	$i-2867$	1	P	31	23789	$i-727$	1	P
12	21719	$k-2986$	$5bd$	D	32	23975	$k-730$	10	P
13	21731	$k-2974$	6	P	33	24178	$k-527$	1	D
14	21768	$k-2937$	10	P	34	24354	$o-2939$	2	P
15	21799	$k-2906$	4	P	35	24386	$k-319$	5	P
16	21837	$k-2868$	10	P	36	24416	$p-2937$	8	P
17	21867	$k-2838$	3	P	37	24448	$o-2877$		
18	21906	$e-1032$	5	D	38	24480	$q-2940$	8	P
19	22081	$k-2624$? (band)	$0bd$	?		24516	$p-2873$	5	P
20	22210	$e-728$	12	P	39	(Hg)	$q-2872$	..	..

$\Delta\nu$ (cm.$^{-1}$)	197	320	526	728	1030	1117	1174	1460
Intensity	$6b$	5	2	12	5	1	$1b$	$6b$
ρ	D	P	D	P	D	P	D	D

$\Delta\nu$ (cm.$^{-1}$)	2624	2838	2870	2910	2940	2975	2988
Intensity	$0bd$	2	10	4	10	6	$5bd$
ρ	?	P	P	P	P	P	D

TABLE II.

Raman Spectrum of Ethyl Borate: $B(OC_2H_5)_3$.

No.	ν	Assignment	Int.	No.	ν	Assignment	Int.
1	19964	*c*—2974	6	21	22525	*c*—413	0*vb*
2	20012	*c*—2926	8	22	22588	*c*—350	1*vb*
3	20041	*c*—2967	5	23	22643	*c*—295	3
4	20070	*c*—2868	5	24	22696	*c*—242	1*b*
5	21450	*c*—1488	3	25	23220	*k*—1485	3
6	21491	*c*—1447	8*b*	26	23260	*k*—1445	8*b*
7	21543	*i*—2973	3*b*	27	23317	*k*—1388	0
		c—1395		28	23373	*k*—1332	2
8	21587	*i*—2929	4	29	23426	*k*—1279	5
9	21615	*i*—2901	3	30	23465	*i*—1051	0
		c—1323		31	23578	*i*—938	0
10	21655	*i*—2861	5	32	23614	*k*—1091	5*b*
		c—1283		33	23654	*k*—1051	5
11	21728	*k*—2977	12	34	23758	*k*—947	3*b*
12	21772	*k*—2933	15	35	23812	*k*—893	4
13	21805	*k*—2900	8*b*	36	23895	*k*—810	1
14	21842	*k*—2863	10*b*	37	23985	*k*—720	4*b*
		c—1096		38	24314	*o*—2979	3
15	21889	*c*—1049	7	39	24358	*o*—2935	3
16	21991	*c*—947	5	40	24378	*p*—2975	2
17	22048	*c*—890	6	41	24417	*p*—2936	8*b*
18	22130	*c*—808	1			*q*—2961	
19	22215	*c*—723	6*b*	42	24457	*q*—2931	8
20	22407	*c*—531?	0*vb*				

$\Delta\nu$ (cm.$^{-1}$)	242	295	350	413	531?	722	809	892	947	1050	1092
Intensity	1*b*	3	1*vb*	0*vb*	0*vb*	6*b*	1	5	4*b*	6	5*b*

$\Delta\nu$ (cm.$^{-1}$)	1280	1328	1390	1446	1486	2864	2898	2932	2975
Intensity	5	2	1	8*b*	3	8	8	15	10

TABLE III.

Raman Spectrum of Boron Tri-Bromide: BBr_3

No.	ν	Assignment	Int.	No.	ν	Assignment	Int.
1	22139	*c*—799	0*d*	8	24239	*i*—277	$\frac{1}{2}$
2	22188	*c*—750	0	9	24366	*i*—150	0
3	22564	*c*—374	0	10	24426	*k*—279	7
4	22659	*c*—279	10	11	24552	*k*—153	5
5	22785	*c*—153	8	12	24857	*k*—152	2
6	23088	*c*—150	5	13	24986	*k*—281	1
7	23222	*c*—284	4				

$\Delta\nu$ (cm.$^{-1}$)	151	280	374	750	799
Intensity	8	10	0	0	0*d*

Boric Acid : B $(OH)_3$: $\Delta\nu$ = 875 cm.$^{-1}$

4. *Discussion of Results.*

Methyl and Ethyl Borates.—The Raman spectra of a few organic borates, including the two under consideration, have been published recently by Joglekar and Thatte[1]. However, as the following table will show, a strange and surprising disagreement is observed between the author's results and those of the previous workers.

TABLE IV.

Methyl borate		Ethyl borate	
Author	Joglekar & Thatte	Author	Joglekar & Thatte
197 (6*b*)		242 (1*b*)	240 (1)
318 (5)		295 (3)	273 (1)
	488 (0)	350 (1*vb*)	323 (1)
526 (2)		413 (0*vb*)	
728 (12)	710 (4)		495 (1)
	860 (0)	531 (0*vb*)?	557 (2)
1030 (5)	1028 (2)		615 (0)
1117 (1)	1112 (2)	722 (6*b*)	727 (2)
1174 (1*b*)		809 (1)	
1460 (6*b*)	1459 (3)		855 (0)
	1563 (0)	892 (5)	890 (2)
	1753 (1)	947 (4*b*)	941 (0)
	1959 (0)	1050 (6)	1055 (2)
	2058 (1*d*)	1092 (5*b*)	
2624 (0*bd*)?			1113 (1)
2833 (2)			1160 (3)
2870 (10)			1210 (0)
	2898 (1)	1280 (5)	1289 (0)
2910 (4)		1328 (2)	
2940 (10)	2940 (1)		1355 (0)
2975 (6)		1390 (1)	
2988 (5*bd*)		1446 (8*b*)	1457 (3)
	3020 (1)	1486 (3)	
			1829 (0)
			1867 (0)
		2864 (8)	
		2898 (8)	
		2932 (15)	2930 (0)
		2975 (10)	2977 (0)
			3040 (0)
			3118 (0)

There is little doubt that the results of Joglekar and Thatte are vitiated by large errors of measurement and even more so by wrong assignments. Of the four characteristic frequencies 710, 1112, 1959 and 2058 assigned by them for methyl borate, the latter two have no existence. As will be pointed out

[1] M. S. Joglekar and V. N. Thatte, *Z. f. Phys.*, 1936, **98**, 692.

below, the four characteristic frequencies of this substance are 197, 320, 526 and 728. A glance at the photograph of the Raman spectrum of methyl borate reproduced in the Plate will show at once that allowing for the errors of measurement, the Raman lines 1959 (0) and 1563 (0) given by Joglekar and Thatte are nothing but the Stokes and anti-Stokes Raman frequency $\Delta\nu = 197$ cm.$^{-1}$ excited by the mercury line λ 4358. Apart from these mistakes, it appears that a number of faint mercury lines in the region λ 4916 have been classified by these authors as Raman lines. In view of what has been said above, it would therefore seem highly desirable to take up a re-investigation also of the remaining four borates (butyl, amyl, iso-amyl and phenyl) studied by them.

The polarisation photograph of methyl borate reveals some very interesting features. If for a moment we overlook the hydrogen frequencies, say above 1100 cm.$^{-1}$, then we might as a first approximation consider the molecule of methyl borate, $B(OCH_3)_3$ as somewhat analogous to the general type XY_3. Such a molecule can have two types of symmetry, C_{3v} or D_{3h} according as the structure is pyramidal or coplanar. In the former case of which the tri-halides of phosphorus and arsenic are examples, there are two totally symmetric and two doubly degenerate vibrations, all the four being active in the Raman effect. The following table gives a comparison of the intensity and polarisation characters of the four lowest frequencies in the Raman spectrum of $B(OCH_3)_3$ with the Raman spectrum of PCl_3 :—

$B(OCH_3)_3$	$\Delta\nu$ ..	197 (6*b*)	320 (5)	526 (2)	728 (12)
	ρ ..	D	P	D	P
PCl_3	$\Delta\nu$ ..	190 (10)	258 (10)	484 (2)	511 (10)
	ρ* ..	·90	·29	·86	·14

The normal vibrations of the pyramidal XY_3 type of molecule have been discussed by Dennison[2] and Bhagavantam.[3] The characteristic determinant for the vibrational frequencies is given by Dennison in the form of the equation

$$\left[l^2 - \left(3a + \tfrac{1}{3} + \frac{\beta}{\mu}\right) l + \frac{3a\beta}{\mu}\right] \times \left[l^2 - \left(\tfrac{3}{2}\, a + \tfrac{1}{6} + \frac{b}{6\mu}\right) l + \frac{ab}{4\mu}\right]^2 = 0$$

* J. Cabannes and A. Rousset, *Ann. de Phys.*, 1933, **19**, 272.

[2] D. M. Dennison, *Phil. Mag.*, 1926, **1**, 195.

[3] S. Bhagavantam, *Ind. Jour. Phys.*, 1930, **5**, 74.

where

$$l = \frac{m(\beta+\frac{1}{3})}{k'}\lambda \qquad \mu = \frac{M}{3m+M}$$

$$a = \frac{k}{k'}(\beta+\tfrac{1}{3}) \qquad b = 1 + 6\mu\beta$$

$$\beta = \frac{c^2}{a^2} \qquad \nu_i = \frac{1}{2\pi}\sqrt{\lambda_i}$$

Here, m and M denote the masses of the Y- and X-atoms, a the normal distance of the Y- atoms from each other, and c the normal distance of the X-atom from the plane of the Y-atoms. The equation consists of two parts, of which the first part gives the frequencies of the totally symmetrical modes, while the second gives the doubly degenerate frequencies. Three constants k, k' and β enter into the equation, of which β is determined purely by the geometry of the molecule ; k denotes the force between two Y-atoms, and k' the force between the X-atom and a Y-atom. Assuming three known frequencies of the molecule, it is possible to make an estimate of these three constants, as well as the magnitude of the fourth frequency. This procedure has been adopted by Dennison in the case of ammonia, and Bhagavantam has applied it for a number of tri-chlorides. We give below the values of β, k and k', and also the magnitude of the observed and calculated frequencies for the molecule $B(OCH_3)_3$, the group (OCH_3) being treated as a single unit. The corresponding values for PCl_3 given by Bhagavantam are also added for comparison.

Substance	β	$k.10^{-4}$	$k.'10^{-4}$		ν_1	ν_2	ν_3	ν_4
$B(OCH_3)_3$	0·4	7·05	16·6	obs.	728	320	526	197
				cal.	722	323	522	228
PCl_3	0·224	7	19	obs.	511	258	484	190
				cal.	498	255	500	178

A comparison with the Raman spectrum of iso-butane, $H.C.(CH_3)_3$ also reveals many points of similarity. The four frequencies listed above have their analogues also in the Raman spectrum of iso-butane. Similarity might also be expected with the Raman spectrum of tri-methyl-amine, $N.(CH_3)_3$ which is at present being investigated by the author. Indeed, the simplicity of its spectrum is remarkable, when one considers the apparent complexity of the molecule of methyl borate. The depolarised frequency 1174 occurs also in the spectrum of iso-butane, and is probably one of the

characteristic vibrations of the CH_3 group in these molecules. The frequencies 1030 and 1117 are, perhaps, to be ascribed to the vibrations of the $-O.CH_3$ group. The remaining frequencies arise, of course, from the vibrations of the hydrogen atoms.

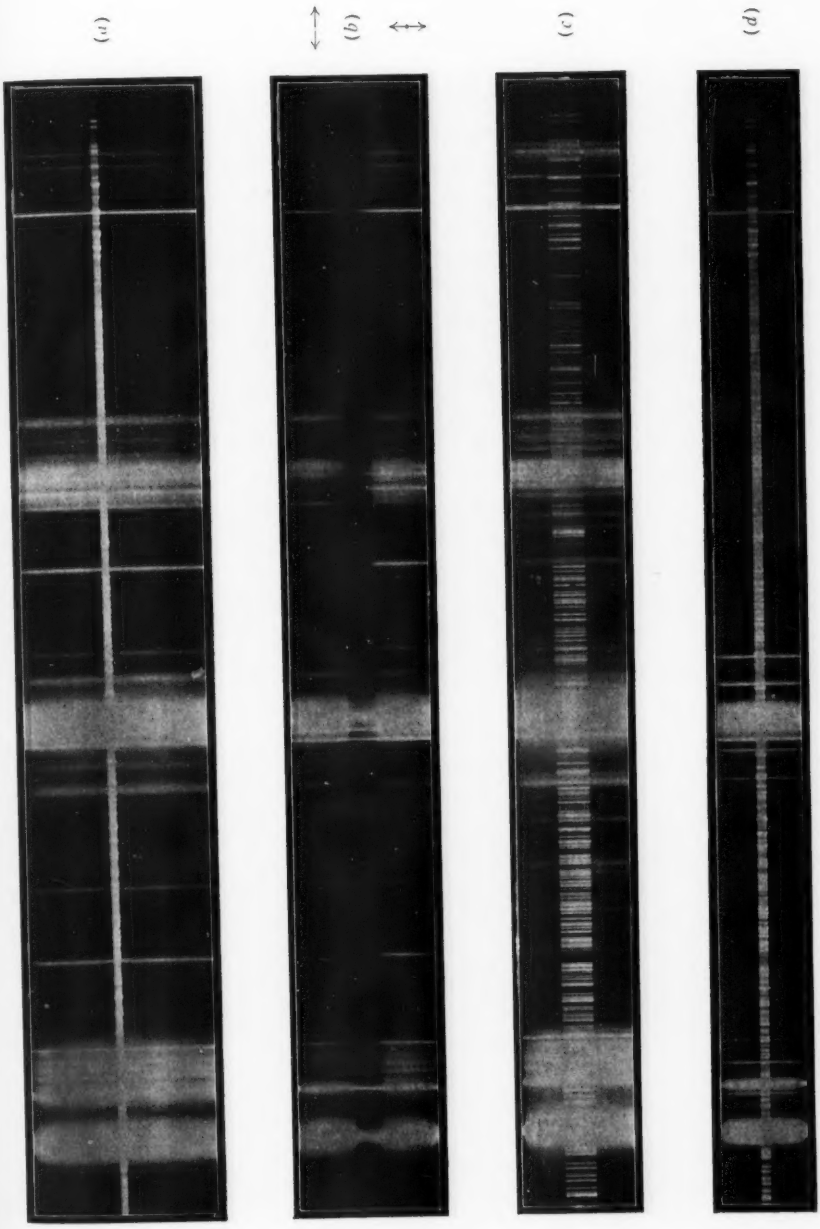
The spectrum of ethyl borate is much more complicated, and apparently shows no such simple regularity. It was therefore considered not worthwhile to investigate the polarisation characters of the Raman lines in this case. It does not seem profitable to enter into a discussion of the frequencies of this substance since any such discussion is bound to be greatly conjectural. The frequency $\Delta\nu = 722$ of ethyl borate corresponds perhaps to the frequency $\Delta\nu = 728$ cm.$^{-1}$ of methyl borate, but unlike the latter which is sharp and very intense, the former is broad and much less intense. In spite of the larger number of hydrogen atoms, it is remarkable that the number of hydrogen lines in the region $\Delta\nu \lesssim 3000$ cm.$^{-1}$ is even less than in the case of methyl borate.

Boron Tri-Bromide.—The Raman spectrum of this substance is reported here for the first time. The following observation seems worthy of record. The liquid was contained in a tiny Raman tube attached to a small bulb, and was coloured intensely red at the beginning of the exposure so that the exciting lines λ 4046 and λ 4358 of the mercury arc were completely absorbed. However, after about 12 hours exposure between two intense pyrex mercury arcs, the liquid in the Raman tube was found to have become quite transparent. Apparently, the colour was due to dissolved bromine which distilled back into the bulb on account of the slight rise of temperature of the liquid in the Raman tube. After the exposure, when the liquid was removed, it slowly regained the original intense red tinge.

The spectrum obtained after an exposure of about 40 hours is reproduced in the Plate. It shows a striking similarity to the Raman spectrum of BCl_3[4] and consists of two intense lines 151 cm.$^{-1}$ and 280 cm.$^{-1}$ which correspond to the frequencies 255 and 472 found in the spectrum of the tri-chloride. Besides, three other lines of feeble intensity are also recorded whose frequency shifts are 374, 750 and 799 respectively. The line of highest frequency shift is somewhat diffuse, and corresponds to the Raman line 947(0*d*) observed in the tri-chloride. The frequency $\Delta\nu = 374$ remains, however, inexplicable.

The Raman spectra of the tri-halides of boron differ in a striking manner from those of the other tri-halides. In the latter cases, experiment and theory alike go to confirm the pyramidal structure. However, such a structure for the tri-halides of boron appears to be irreconcilable with certain

[4] S. Venkateswaran, *Ind. Jour. Phys.*, 1931, **6**, 275.



Raman Spectra.

(*a*) Methyl borate
(*b*) Methyl borate : polarisation
(*c*) Ethyl borate
(*d*) Boron tri-bromide

known facts. Experiments on dipole moment show that the moment of BCl_3 is vanishingly small. This can be so only if the molecule of BCl_3 is coplanar with the B-atom at the centre of symmetry of the Cl_3 triangle. The molecule will then have the symmetry D_{3h}, and would possess four frequencies, of which three are Raman-active one being totally symmetrical (polarised) and two doubly degenerate (depolarised). The Raman lines 280 of the tri-bromide and 472 of the tri-chloride represent presumably the totally symmetrical vibrations, being the most intense lines in the spectra. Nevertheless, a careful study of the polarisation of the Raman lines of these two substances might perhaps throw further light on their constitution.

The infra-red absorption spectrum of BCl_3 has been studied recently by Cassie[5] but unfortunately the study has not been pushed sufficiently far to enable a definite decision to be made as to the molecular configuration. As he has remarked, a choice between the pyramidal and planar configurations could be made if infra-red observations were available up to 25 μ; this would include the region 470 cm.$^{-1}$ where the most intense Raman line appears, and if the molecule be planar this frequency will be inactive in the infra-red, whereas if the molecule be pyramidal it will be active.

Boric Acid.—The single frequency at 875 cm.$^{-1}$ evidently represents the totally symmetric vibration of the molecule $B(OH)_3$. No other lines could be observed because of the intense background.

In conclusion, the author wishes to express his respectful thanks to Professor Sir C. V. Raman for his kind interest in the present work.

Summary.

The Raman spectra of methyl and ethyl borates have been carefully investigated, and it is found that the Raman frequencies previously reported for these substances require considerable revision. The Raman spectrum of methyl borate in the region of low frequencies shows great similarity to the spectra of the tri-chlorides of phosphorus and arsenic, and this similarity is strikingly brought out by the polarisation characters of the Raman lines. A pyramidal structure is postulated for the $B(OCH_3)_3$ molecule, the group (OCH_3) being treated as a single unit. The observed and calculated frequencies are in fair agreement. The Raman spectrum of boron tri-bromide is reported for the first time, and consists of two very intense lines and three very weak ones. These are compared with the frequencies of the tri-chloride. Only one line was found in the case of boric acid, which is attributed to the totally symmetrical vibration of the molecule.

[5] A. B. D. Cassie, *Proc. Roy. Soc.*, A, 1935, **148**, 87.

THE RAMAN SPECTRA OF CYCLO-PROPANE* AND ETHYLENE OXIDE.

By R. Ananthakrishnan.

(*From the Department of Physics, Indian Institute of Science, Bangalore.*)

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

Special interest attaches to a detailed study of the Raman spectra of cylcopropane and ethylene oxide, because the former is the simplest of the cyclic hydrocarbons, while the latter is the leading member of a whole series of three-membered heterocyclic compounds. The chemically indicated structural similarity of the molecules of these two substances renders the comparative study of their Raman spectra, a matter of some importance. The fact that cyclo-propane is a typical non-polar substance while the molecule of ethylene oxide possesses a permanent dipole moment is, however, a point for consideration. The author has made a careful invsetigation of the Raman spectra of these two substances; the results are embodied in the present paper.

2. Experimental.

The substances were taken from commercial cylinders supplied by the Ohio Chemical and Manufacturing Co., Ltd. Cyclo-propane was labelled 99·5% pure. It was dried, rendered free from dust by passing through a plug of compressed cotton wool and condensed in a slow stream in a tube of thick-walled pyrex glass cooled in a bath of alcohol and carbon-di-oxide snow. When the requisite quantity of liquid had collected, the tube was sealed off. Ethylene oxide was condensed directly from the cylinder; the liquid was distilled a number of times in vacuum before it was used for the experiment. The spectra of the liquids were photographed at room temperature in the usual manner[1] using a Hilger two-prism spectrograph. Both the liquids yielded very intense pictures absolutely free from background.

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*A note to *Nature*, communicated on 6th May 1936, contains the essential results relating to the Raman Spectrum of cyclo-propane described in this paper.

[1] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, A, 1936, 3, 527.

3. *Results.*

The following tables give a comple analysis of the Raman spectra of cyclo-propane and ethylene oxide in the region between λ 4046 and λ 5100. The notations employed are the same as in the author's former papers.

TABLE I.

Raman Spectrum of Cyclo-propane.

No.	ν	Assignment	Int.	Poln.	No.	ν	Assignment	Int.	Poln.
1	19858	*e*—3080	3 *bd*	D	15	22075	*e*—863	8 *b*	D
2	19910	*e*—3028	5	P	16	22203	*e*—735	0 *bd*	D
3	19928	*e*—3010	5	P	17	23201	*k*—1504	0 *s*	P
4	19986	*e*—2952 *f*—3009	1	P	18	23271	*k*—1434	3 *bd*	D
					19	23328	*i*—1188	3 *s*	P
5	20085	*e*—2853	½	P	20	23518	*k*—1187	15	P
6	21436	*i*—3080 *e*—1502	1 *d*	D	21	23654	*i*—862	1 *bd*	D
					22	23841	*k*—864	8 *b*	D
7	21488	*i*—3028	2	P	23	23968	*k*—737	0 *bd*	D
8	21508	*i*—3008 *e*—1430	2	P	24	24210	*o*—3083	1 *bd*	D
					25	24264	*o*—3029	6	P
9	21625	*k*—3080	6 *bd*	D	26	24282	*o*—3011	6	P
10	21678	*k*—3027	10	P	27	24360	*q*—3028	8	P
11	21695	*k*—3010	10	P	28	24378	*q*—3010	8	P
12	21751	*e*—1187 *k*—2954	15	P	29	24403	*p*—2950	1	P
					30	24434	*q*—2954	2	P
13	21809	*f*—1186	½ *s*	P					
14	21854	*g*—1185 *k*—2851	1 *s*	P					

Δ ν (cm.$^{-1}$)	..	736	863	1187	1434†	1503	2852	2952	3010	3028	3080
Int.	..	0*bd*	8*b*	15	2*b*	0*s*	½	1	10	10	6*bd*
ρ	..	D	D	P	D	P	P	P	P	P	D

† This Raman Band shows a doublet structure.

TABLE II.

Raman Spectrum of Ethylene Oxide.

No.	ν	Assignment	Int.	Poln.	No.	ν	Assignment	Int.	Poln.
1	19876	e—3062	1 d	D	17	23511	k—1494	1 b	P
2	19928	e—3010	5	P	18	23247	i—1269	2	P
3	19977	e—2961	3	P	19	23435	k—1270	15 s	P
4	20022	e—2916	3	P	20	23456	k—1159	2 b	D
5	21448	e—1490	2 b	P	21	23584	k—1121	5	P
6	21508	i—3008	2	P	22	23837	k—868	6 b	D
7	21555	i—2961	1	P	23	23899	k—806	6 b	D
8	21600	i—2916	1	P	24	24233	o—3060	1 d	D
9	21643	k—3062	4 bd	D	25	24283	o—3010	4	P
10	21668	e—1270	15 s	P	26	24346	p—3007	4	P
11	21697	k—3008	10	P	27	24378	o—2915 } q—3010 }	8	P
12	21747	k—2958	6	P					
13	21788	k—2917	8	P	28	24393	p—2960	3	P
14	21815	e—1123	5	P	29	24429	p—2924 } q—2959 }	5	P
15	22069	e—869	8 b	D					
16	22130	e—808	8 b	D	30	24471	q—2918	4	P

$\Delta\nu$ (cm.$^{-1}$) ..	807	869	1122	1159	1270	1492	2917	2960	3008	3062
Int. ..	8b	8b	5	2b	15s	1b	6	6	10	4bd
ρ ..	D	D	P	D	P	D?	P	P	P	D

(s = sharp ; b = broad ; d = diffuse ; P = polarised ($\rho \ll \frac{6}{7}$) ; D = depolarised ($\rho \approx \frac{6}{7}$).

4. Discussion of Results.

(1) *Cyclo-propane.*—The Raman spectrum of cyclo-propane in the liquid state was first studied by Lespieau-Bourguel-Wakeman[2] and later by Kohlrausch-Köppl[3] with practically identical results. The following table gives a comparison of the author's results with those of the latter authors.

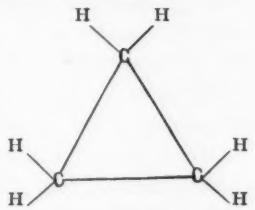
	736	863	1187	1434†	1503	2852	2952	3010	3028	3080
Author	0bd	8b	15	2b	0s	½	1	10	10	6bd
	D	D	P	D	P	P	P	P	P	D
Kohlrausch and Köppl		864	1184	1453				3008	3026	3078
		6b	12	2b				8	8	3b

[2] R. Lespieau, M. Bourguel and R. Wakeman, *Bull. Soc. Chim.*, 1932, **4**, 51–52, 400.

[3] K. W. F. Kohlrausch and F. Köppl, *Z. f. Phys. Chem.*, B, 1934, **26**, 209.

It will be seen that several new lines have been found in the spectrum of this substance. If we leave aside the frequencies above 1400 which presumably owe their origin to those vibrations in which the H atoms are primarily involved, we are left with the three frequencies 736, 863 and 1187.

The absence of a permanent dipole moment for the molecule of cyclo-propane as well as other chemical evidence goes to show that the three carbon atoms of this molecule are at the corners of an equilateral triangle with a pair of H atoms attached to each C atom.



However, as far as the author is aware, neither X-ray nor electron diffraction data are available for the molecule of this substance. In so far as the fundamental frequencies of the carbon ring are concerned, if it is permissible to treat the molecule as a system composed of three identical mass points (herein we ignore the influence of the H atoms on the ring oscillations), then the molecular model has the symmetry C_{3h}. It has two fundamental modes of vibration of which one is totally symmetrical (ω_1) and the other doubly degenerate ($\omega_{2,3}$). According to Placzek's selection rules, the former vibration should give rise to an intense and well-polarised ($\rho \ll \frac{6}{7}$) Raman line, while the latter is forbidden in the Raman effect. Experimental results in the case of cyclo-propane apparently do not seem to support the latter conclusion. There is little doubt that while the intense and well-polarised Raman line at 1187 represents the totally symmetrical vibration ω_1, the broad, intense and depolarised Raman frequency at 863 has to be identified with $\omega_{2,3}$. Kohlrausch and Köppl[4] have suggested that the appearance of $\omega_{2,3}$ in the Raman spectrum of cyclo-propane (liquid) with such great intensity is perhaps due to the perturbation of the symmetry of the molecule. Such a perturbation of the molecular symmetry might also be expected to give rise to a splitting of the doubly degenerate frequency $\omega_{2,3}$ into its two components ω_2 and ω_3. The nature of the deviation from the symmetry of the accepted chemical structure is, however, far from being clear and indeed very difficult to conceive. It is necessary to point out that the influence of the H atoms on the vibrations of the carbon nuclei has to be mathematically

[4] K. W. F. Kohlrausch and F. Köppl, *Loc. cit.*

examined before too much emphasis can be laid on this hypothetical postulate. Whether it is justifiable to identify the frequencies 736 and 863 with ω_2 and ω_3 respectively, remains an open question. It is significant that the frequency 736 which is quite feeble in the case of cyclo-propane corresponds to a strong Raman line that occurs in all the substituted cyclo-propanes.[5]

Two possible alternatives have been suggested by Kohlrausch and Köppl, that might be responsible for a possible perturbation of the symmetry of the cyclo-propane molecule. The first is the influence of the neighbouring molecules which might be expected to be quite appreciable in the liquid state. That this view is invalid will be shown in a subsequent section. The second alternative is the inherent asymmetry of the carbon valencies. In this connection, the above authors have quoted certain results of Cabannes and Rousset[6] for the depolarisation of the degenerate vibrational Raman lines of $CHCl_3$ and $CHBr_3$. Cabannes and Rousset reported to have found that in the case of both these substances, two of the degenerate frequencies exhibited a depolarisation factor clearly inferior to the theoretical value $\frac{6}{7}$. They attributed this deviation to a removal of the degeneracy caused by the asymmetry of the carbon valencies. Such an explanation appears, however, to be far-fetched, and indeed, inasmuch as the polarisation measurements of Simons for the vibrational Raman lines of $CHCl_3$ are in conformity with Placzek's theroy,[7] the matter demands re-examination. It might be added that the author has recently found a case[8] (water) in which the polarisation measurements of Cabannes and Rousset appear to be erroneous.

If we adopt the central force system (Dennison), the frequencies ω_1 and $\omega_{2,3}$ of the equilateral triangle are connected by the relation $\frac{\omega_1}{\omega_{2,3}} = \sqrt{2} = 1{\cdot}414$. If we put $\omega_1 = 1187$ and $\omega_{2,3} = 863$ we find that $\frac{\omega_1}{\omega_{2,3}} = 1{\cdot}375$. The agreement, though not good, is not very unsatisfactory.

(2) *Ethylene oxide.*—The Raman spectrum of this substance in the liquid state was investigated first by Lespieau and Bourguel.[9] Recently Timm and Mecke[10] have made a study of its Raman spectrum. The following table gives a comparison of the author's results with those of the previous workers.

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[5] See R. Lespieau, M. Bourguel and R. Wakeman, *Loc. cit.*

[6] J. Cabannes and A. Rousset, *Ann. de Phys.*, 1933, **19**, 229.

[7] See G. Placzek, *Handbuch der Radiologie, Quantenmechanik der Materie und Strahlung*, Teil 2, 1934, S. 310.

[8] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, A, 1936, **3**, 201.

[9] R. Lespieau and M. Bourguel, *Bull. Soc. Chim., France*, 1930, **47**, 1365.

[10] B. Timm and R. Mecke, *Z. f. Phys.*, 1935, **97**, 221.

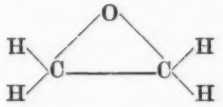
Author	807	869	1122	1159	1270	1492	2917	2960	3008	3062
	8*b*	8*b*	5	2*b*	15*s*	1*b*	6	6	10	4*bd*
	D	D	P	D	P	D	P	P	P	D
Lespieau-Bourguel	808	869	1119		1269		2917	2959	3009	
	6	6	3		6		3	3	3	
Timm and Mecke	807	873	1128		1268		2924	2970	3008	3047
	0	1	1		5		1	1	4	1

Two new lines at 1159 and 1492 have been found in the spectrum of this substance. An examination of the table reveals considerable discrepancy in the relative intensities of the Raman lines reported by the various investigators. The discrepancy is very great indeed between the author's results and those of Timm and Mecke. While in the present investigation, it is found both visually as well as from the microphotometric records that the pair of broad Raman lines at 807 and 869 are of equal intensity, Timm and Mecke have found considerable difference in intensity between these two lines. It should be recalled, in this connection, that while the author's photographs were taken at the room temperature (25°), Timm and Mecke studied the Raman spectrum of the liquid at $-10°$. Many instances are known where the relative intensity of the Raman lines of polar substances are considerably influenced by temperature. Liquid ammonia which has been investigated by Daure at $-40°$ and by Bhagavantam at room temperature affords a striking example. The Raman bands of this substance in the $3\,\mu$ region show a remarkable intensity variation with temperature. It is therefore not improbable that similar intensity changes might also be exhibited by the Raman spectrum of ethylene oxide. The author hopes to return to this problem on a later occasion.

Of the fifteen fundamental frequencies of the molecule C_2H_4O, ten have been recorded in the present investigation. Just as in the case of cyclo-propane, we can classify the frequencies of the molecule of ethylene oxide into two groups. The depolarised Raman frequencies 807 and 869 and the intense and polarised line at 1270 represent the fundamental ring frequencies. The remaining seven frequencies have their origin primarily in the vibrations

of the H atoms. Mecke's remark[11] that the δ (C—H) frequency in the neighbourhood of 1450 is absent in the case of ethylene oxide is not true.

From his experiments on electron diffraction, Wierl[12] concluded that the molecule of ethylene oxide possesses the configuration



with $d_{C-C} \simeq d_{C-O} = 1{\cdot}49$ Å, so that the two C-atoms and the O-atom lie at the corners of an, at least approximately, equilateral triangle. For the sake of simplicity we consider the molecule of ethylene oxide as a system composed of three mass points (with masses 16, 14, 14) placed at the corners of an isosceles triangle. The model has the symmetry C_{2v}. If we follow the treatment given by Dennison[13] for the normal vibrations of such a system, we can calculate from the observed frequencies the magnitude of the C–C and C–O force constants (k and k') as well as the valence angle subtended at the oxygen atom (2α).[14] The results of such a calculation are given in the table below.

ω_1	ω_2	ω_3	k	k'	2α
807	1270	869	$5{\cdot}59 \times 10^5$	$3{\cdot}69 \times 10^5$	51°
			$3{\cdot}22 \times 10^5$	$4{\cdot}95 \times 10^5$	22°
869	1270	807	**$5{\cdot}16 \times 10^5$**	**$3{\cdot}9 \times 10^5$**	**72°**
			$3{\cdot}02 \times 10^5$	$5{\cdot}04 \times 10^5$	44°

5. Raman Spectrum of Cyclo-propane Vapour.

Very few substances have been investigated by the method of light scattering in all the three states of aggregation. Those substances whose Raman spectra have been studied in both the liquid and vapour states belong mostly to the polar group. Indeed, it might be expected that only in such

[11] B. Timm and R. Mecke, *Loc. cit.*

[12] R. Wierl, *Ann. der Phys.*, 1932, **13**, 453.

[13] D. M. Dennison, *Phil. Mag.*, 1926, **1**, 195.

[14] N. G. Pai (*Curr. Sci.*, 1934, **2**, 386) has calculated $2\alpha = 64°$, assuming 810, 865, and 1151 as the fundamental frequencies. The third fundamental frequency (1151) assumed by this author is incorrect.

cases, change of state would be accompanied by modifications in the Raman spectra. The examination of cyclo-propane in the vapour state, however, appeared to be of interest, in order to see whether the depolarised Raman line at 863 cm.$^{-1}$ is also present in the vapour spectrum.

A few c.c. of the liquid were condensed in a thick-walled pyrex glass tube, about 10 inches long and 2 cm. internal bore. The tube was sealed off so that at the room temperature it contained the vapour at the saturation pressure (7 to 8 atmospheres). The vapour was illumined by means of two intense pyrex mercury arcs, and the scattered radiation was photographed using a Fuess spectrograph. An exposure of 40 hours gave a tolerably good picture, in which the Raman lines 863 and 1187 excited by the mercury lines λ 4046 and λ 4358 were recorded very clearly. Besides, the two hydrogen frequencies 3010 and 3028 excited by λ 4046 were also clearly recorded. A microphotometric record of the vapour spectrum is given at the end of the paper, and the various lines are indicated by the corresponding frequency shifts.

The Raman line at 863 cm.$^{-1}$ which is broad and intense in the spectrum of liquid cyclo-propane, appears as a very diffuse line in the spectrum of the vapour. The existence of this frequency in the spectrum of the vapour clearly shows that its presence in the liquid spectrum cannot be attributed to the perturbation of symmetry of the cyclo-propane molecule due to the influence of its neighbours. Indeed, the great intensity of this line, as well as the non-polar nature of the molecule rules out such an explanation. It is quite definite that the occurrence of this deformation frequency in the Raman spectrum of cyclo-propane is an inherent feature of the molecule itself.

A striking difference is, however, noticed between the Raman spectrum of the liquid and of the vapour when one compares the relative intensity of the Raman lines 3010 and 3028. In the liquid, these two lines are of equal intensity, and the intensity of either is less than that of the Raman line $\Delta\nu = 1187$. In the vapour spectrum the Raman line 3010 is found to have become considerably weaker, while $\Delta\nu = 3028$ has gained in intensity and is more intense than the Raman line 1187. Such a reversal of intensity, from liquid to vapour, is very surprising in the case of a non-polar molecule, and might perhaps be connected in a general way with the mutual influence of the hydrogen atoms of neighbouring molecules in the liquid state.

In conclusion, the author wishes to express his respectful thanks to Professor Sir C. V. Raman for his kind interest in the present work.

Summary.

The Raman spectrum of cyclo-propane has been investigated at the room temperature both in liquid and vapour states. Ten frequencies have been recorded in the spectrum of the liquid of which four are reported for the first time. The state of polarisation of the vibrational Raman lines has also been studied. The four intense Raman lines of the liquid (863, 1187, 3008 and 3028) have also been recorded in the spectrum of the vapour. The significance of the presence of the frequency $\Delta \nu = 863$ in the spectrum of the vapour is pointed out. The relative intensity of the Raman lines 3008 and 3028 is considerably modified in passing from the liquid to the vapour state. The Raman spectrum of ethylene oxide also shows ten frequencies of which two have not been previously recorded. The spectrum shows great similarity to that of cyclo-propane. The polarisation characters of the Raman lines have been determined, and the molecular configuration discussed.

[Note.—Since the above work was completed, a paper on the Raman Spectrum of Cyclo-propane, by Harris, Ashdown and Armstrong, has appeared (*J.A.C.S.*, May 1936, p. 852). These authors have used the mercury line λ 2536 as the exciting source, and have obtained all the frequencies reported by the author for liquid cyclo-propane. Besides, they have found two very weak frequencies, 382 and 1873, and a third one of medium intensity at 1022. From the intensity estimates given by them, the latter line appears to have almost the same intensity as the hydrogen frequencies 3008 and 3028. This line is not observed in any of the author's plates. The fact that the more feeble Raman lines (736, 1503, 2852, 2952) have been clearly recorded by the author, renders the reality of this frequency rather doubtful. The American authors have found only one frequency (1187) in the spectrum of cyclo-propane vapour.]

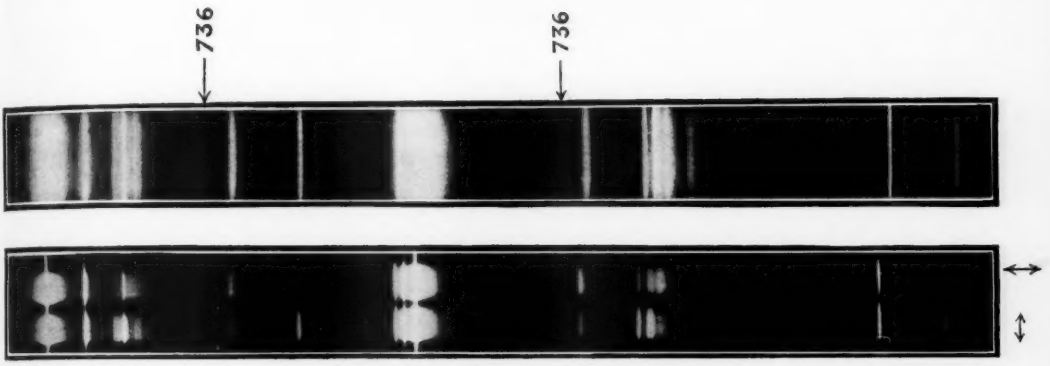


FIG. 1. Raman Spectrum of Cyclo-propane.

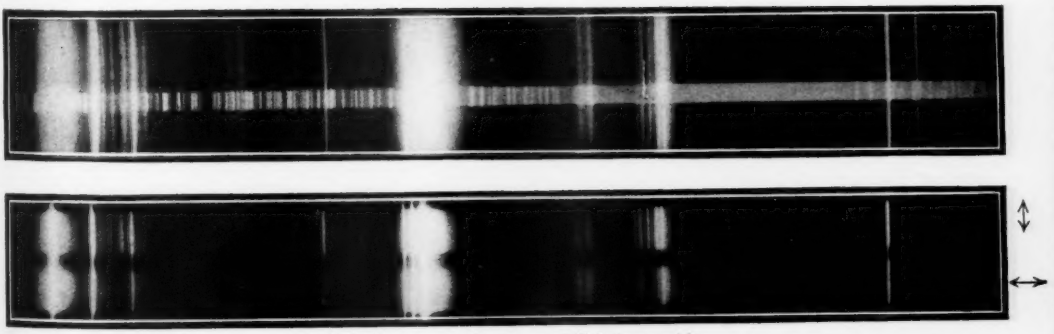


FIG. 2. Raman Spectrum of Ethylene oxide.

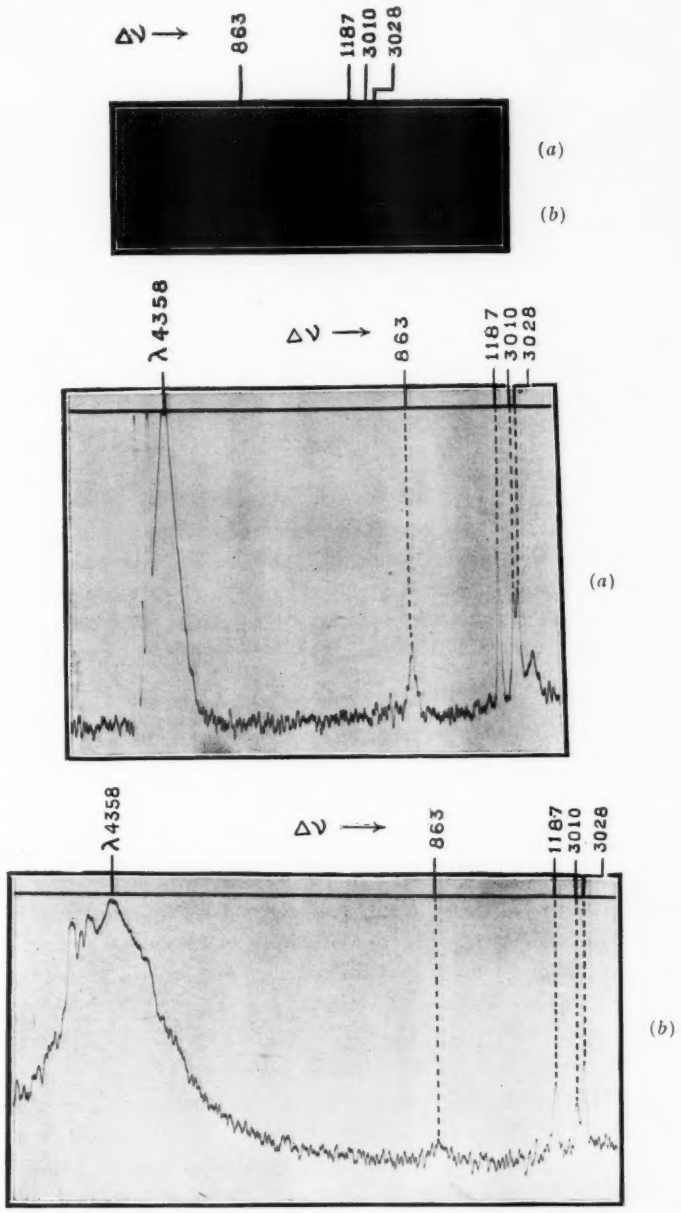


FIG. 3. Microphotometric records of the Raman Spectrum of cyclo-propane showing intensity changes of the Raman lines in passing from the liquid to the vapour state. (*a*) liquid. (*b*) vapour.

THE KINETICS OF HETEROGENEOUS ORGANIC REACTIONS (II): THE REACTION BETWEEN BENZYL CHLORIDE AND SOLID SILVER NITRATE IN THE PRESENCE OF INERT DILUENTS.

By M. V. Nabar
and
T. S. Wheeler.
(From the Department of Chemistry, Royal Institute of Science, Bombay.)

Received May 30, 1936.

Introduction.

In a previous paper[1] the authors have shown that when benzyl chloride and solid silver nitrate react in the absence of solvents and diluents, the rate of reaction is independent of the amount of benzyl chloride, but is proportional to the surface of silver nitrate present. The course of the reaction in the presence of ether (sulphuric), chloroform and carbon tetrachloride has now been investigated; results similar to those in Part I have been obtained.

Materials Used.

Silver Nitrate.—This was of the same quality and prepared in the same way as described in the previous paper; the average particle size was the same as that of the sample (M) used before.

Benzyl Chloride.—Kahlbaum's benzyl chloride "purest" was used as before.

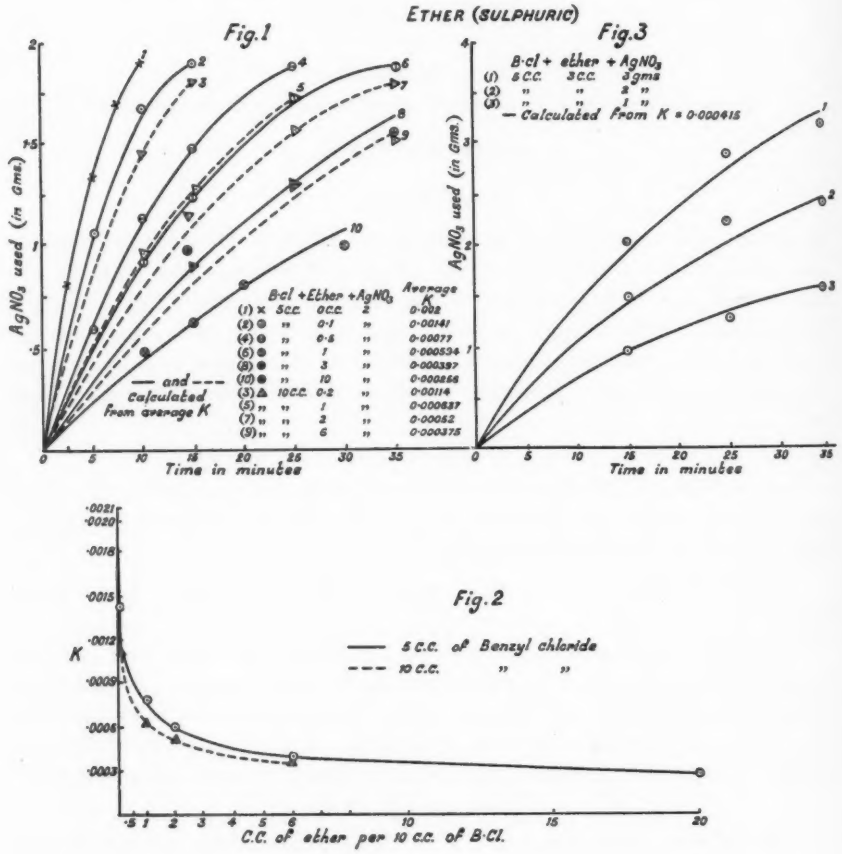
Diluents.—Kahlbaum's ethyl ether anhydrous, distilled over sodium, for analytical purposes, Merck's chloroform P.B., double distilled over phosphorous pentoxide and Merck's extra pure carbon tetrachloride, distilled over phosphorous pentoxide were used. Kahlbaum's chloroform and carbon tetrachloride gave the same type of results in check experiments.

Experimental Methods.

The diluent used, measured by a pipette was added to the benzyl chloride before placing in the air thermostat adjusted to $35° \pm \cdot 2$ C. The experimental technique was otherwise the same as before, except that in presence of diluents, it was not found necessary to use a wet cloth to control the reaction temperature.

Experimental Results and Discussion.

Ether.—Fig. 1 shows the effect of addition of ether. It acts as a strong inhibitor, a definite result being obtained even with 0·1 c.c., with 5 c.c. of benzyl chloride. With a constant quantity of silver nitrate and the same mixtures of benzyl chloride and ether, doubling the quantity of liquid taken, slightly increases the inhibiting effect.


ETHER (SULPHURIC)
Fig.1
AgNO3 used (in cms.)
Time in minutes
— and --- Calculated From average K
B·cl + Ether + AgNO3 Average K
(1) × 5 c.c. 0 c.c. 2 0·002
(2) ● " 0·1 " 0·00141
(4) ● " 0·5 " 0·00077
(5) ● " 1 " 0·000534
(8) ● " 3 " 0·000397
(10) ● " 10 " 0·000256
(3) △ 10 c.c. 0·2 " 0·00114
(5) " " 1 " 0·000637
(7) " " 2 " 0·00052
(9) " " 6 " 0·000375
Fig.3
B·cl + ether + AgNO3
(1) 5 c.c. 3 c.c. 3 gms
(2) " " 2 "
(3) " " 1 "
— Calculated From K = 0·000415
AgNO3 used (in gms.)
Time in minutes

The equation developed in the previous paper

$$K = \frac{3}{tS}\left\{1 - \frac{X^{\frac{1}{3}}}{A^{\frac{1}{3}}}\right\} \quad \ldots \quad (1)$$

where t = time in minutes ;
S = surface area of silver nitrate ;
X = amount of silver nitrate left ;
A = initial amount of silver nitrate ;
fits the curves moderately well.

As with sample (M) before, S was 92·2 sq. cms. throughout this set of experiments. The points show the experimental results and the lines the calculated values [equation (1)] using the values of K indicated.

Fig. 2 shows a plot of values of K for 2 gms. of silver nitrate against the quantity of ether taken per 10 c.c. of benzyl chloride. The curves for 5 c.c. and 10 c.c. of benzyl chloride lie close toegther.

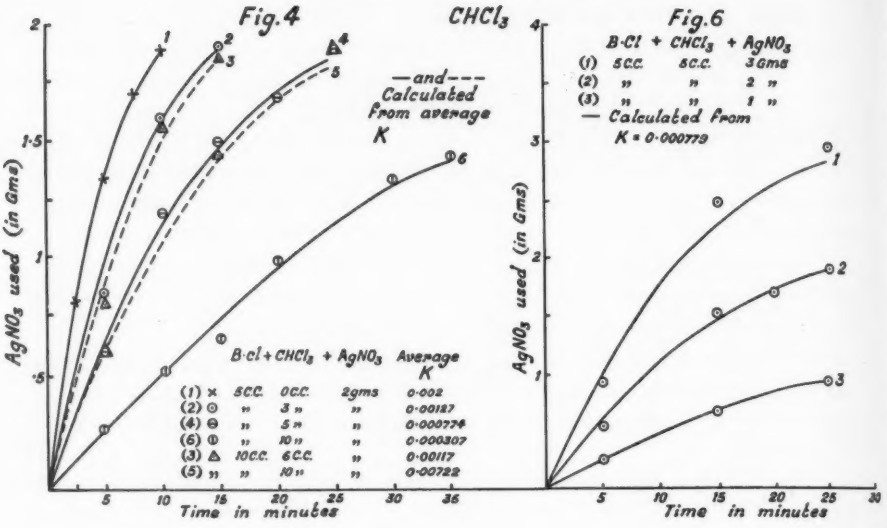
The effect of addition of ether is great initially but then falls off. This can be explained by assuming that ether is adsorbed on the surface of silver nitrate, and that saturation of this surface is attained with small quantities of ether.

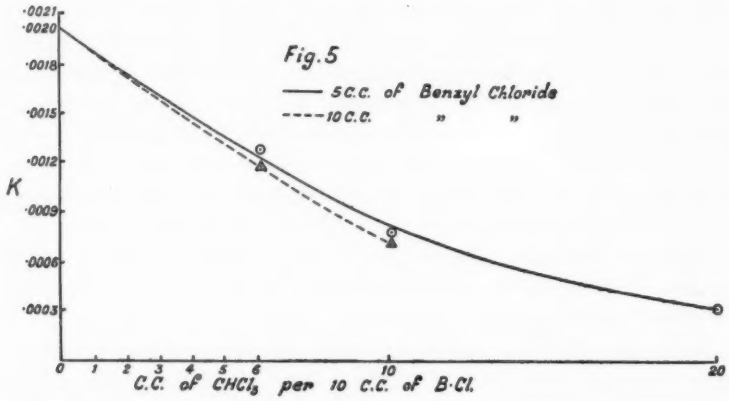
Fig. 3 shows experiments with a constant quantity of benzyl chloride and ether, with varied amounts of silver nitrate. The curves are calculated using equation (1) and as will be seen, for one value of K they pass fairly well through all the experimental points. From these results it would appear that the nature of the reaction is the same as when the diluent is absent.[2] Benzyl chloride is adsorbed on the surface of silver nitrate particles and the amount of adsorption does not depend greatly on the concentration of benzyl chloride in the mixture of benzyl chloride, ether and benzyl nitrate. There is, therefore, always a constant concentration of benzyl chloride on the silver nitrate surface, and the rate of reaction is consequently proportional to the surface of silver nitrate present. The ether while not changing the nature of the reaction causes it to proceed at a definitely slower rate, possibly because it too is adsorbed on the surface of silver nitrate.

Chloroform.—The curves (Fig. 4) with chloroform are of the same type as those obtained with ether, but the inhibition is less. Here again the lines which show the values calculated from equation (1) pass well through the experimental points.

The effect of addition of chloroform on the value of K is shown in Fig. 5. The initial effect is not so marked as with ether.

Fig. 6 shows the experiments with a constant quantity of benzyl chloride and chloroform with definite amounts of silver nitrate. The lines are calculated from equation (1) and here also they pass well through the experimental points, for one value of K.





Carbon Tetrachloride.—The curves (Fig. 7) obtained with carbon tetrachloride are of the same type as obtained with ether and chloroform. Here also the inhibition is less than that with ether. The lines showing the calculated values [equation (1)] pass well through the experimental points.

The effect of the addition of carbon tetrachloride on the value of K is shown in Fig. 8.

Fig. 9 shows the experiments with a constant quantity of benzyl chloride and carbon tetrachloride with different amounts of silver nitrate.

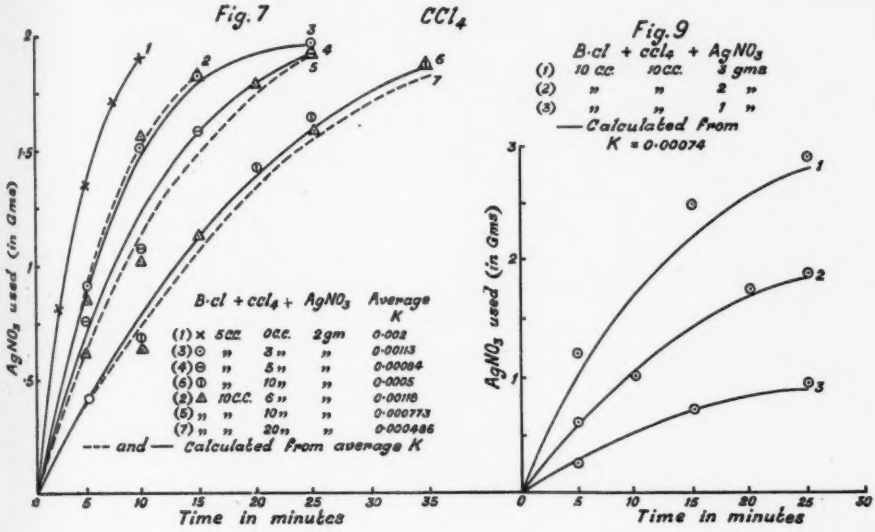
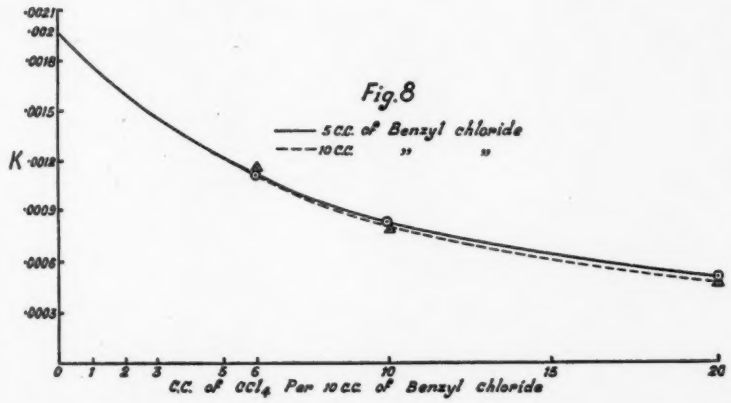


Fig. 7
CCl_4
$AgNO_3$ used (in Gms)
Time in minutes
B·cl + ccl_4 + $AgNO_3$ Average K
(1) × 5 cc. 0 cc. 2 gm 0·002
(3) ⊙ " 3 " " 0·00113
(4) ⊖ " 5 " " 0·00084
(5) ⊕ " 10 " " 0·0005
(2) △ 10 c.c. 6 " " 0·00118
(5) " " 10 " " 0·000773
(7) " " 20 " " 0·000486
--- and — Calculated from average K
Fig. 9
B·cl + ccl_4 + $AgNO_3$
(1) 10 cc. 10 cc. 3 gms
(2) " " 2 "
(3) " " 1 "
— Calculated from K = 0·00074
$AgNO_3$ used (in Gms)
Time in minutes



Here again the lines calculated from equation (1) using one value of K pass through the experimental points for 1 and 2 gm. of silver nitrate; for 3 gm. of silver nitrate the agreement is not good.

It should be understood that while the equation given above satisfies the experimental results moderately well the possibility of other interpretations of the experimental results should not be excluded.

Summary.

(1) The kinetics of the reaction between benzyl chloride and solid silver nitrate has been studied in the presence of dry ethyl ether, chloroform and carbon tetrachloride.

(2) All these diluents inhibit the reaction, the effect of ether being most marked.

(3) The rate of reaction is proportional to the surface of silver nitrate present ; it is independent of the initial amount of a given mixture of benzyl chloride and diluent taken.

(4) The experimental results can be reproduced by a kinetic equation based on the assumption that the rate of reaction for a given initial mixture of benzyl chloride and diluent depends only on the surface of the silver nitrate present.

(5) The effect of the diluent may be due to the adsorption on the surface of the silver nitrate.

REFERENCES.

1. Nabar and Wheeler, *Proc. Ind. Acad. Sci.*, 1935, **2**, 265.
2. See Part I, *loc. cit.*

AGEING OF SURFACES OF SOLUTIONS—II.

Activated Accumulation of Solute Molecules.

By K. S. Gururaja Doss.

(From the Department of Chemistry, Central College, Bangalore.)

Received February 28, 1936.

Introduction.

The ageing of surfaces of solutions has been investigated by a number of workers by studying the variation of surface tension with time. They have all* employed methods which either involve contact angles or in which the surface is considerably disturbed. A critical review of the available methods of determining surface tension revealed that the surface pressure technique of Langmuir and Adam was most suitable for the study of ageing of surfaces of solutions. The present investigations show that this technique is extremely useful in elucidating the behaviour of molecules at interfaces.

Experimental.

A torsion balance similar to that used by Lyons and Rideal[2] in their work on condensed films was employed for surface pressure measurements. The trough and the barriers were of glass. The float was of paraffined aluminium foil and the leakage was prevented by using copper foil ribbons. The barriers and the edge of the trough were waxed with high grade paraffin. Chemicals of high grade purity supplied by Kahlbaum were used.

The fall in surface tension of 0·002 *molar solution of benzopurpurin with time.*—The following method was adopted for measuring the variation in surface tension. The trough was filled with the solution and the surfaces on either side of the float were cleared by moving the barriers. The surface on one of the sides of the float was allowed to age for forty-eight hours. It was then found that the next half an hour of ageing did not produce any appreciable change in the surface tension of the aged surface as judged by the measurements of surface pressure against a freshly generated surface on the other side of the float. This aged surface was taken as the standard of reference and the ageing of the surface on the other side of the float was studied by noting, from time to time, the values of the surface pressure. An experiment was also conducted in which an one-minute old surface

* The only exception seems to be Adam, who has studied the same by the sessile bubble method (1). Details of the experimental results have not yet been published.

was used as a reference. To start with both the surfaces were fresh. To take a reading, the reference surface was cleared by barriers and the surface pressure read exactly a minute later. The laboratory conditions were such, that there was little atmospheric contamination. For, it was found that a fresh surface of water could be left for hours together without any detectable change of surface tension. Table I and Fig. 1 illustrate the nature of the variation of surface tension of 0·002 M benzopurpurin 6 B with time.

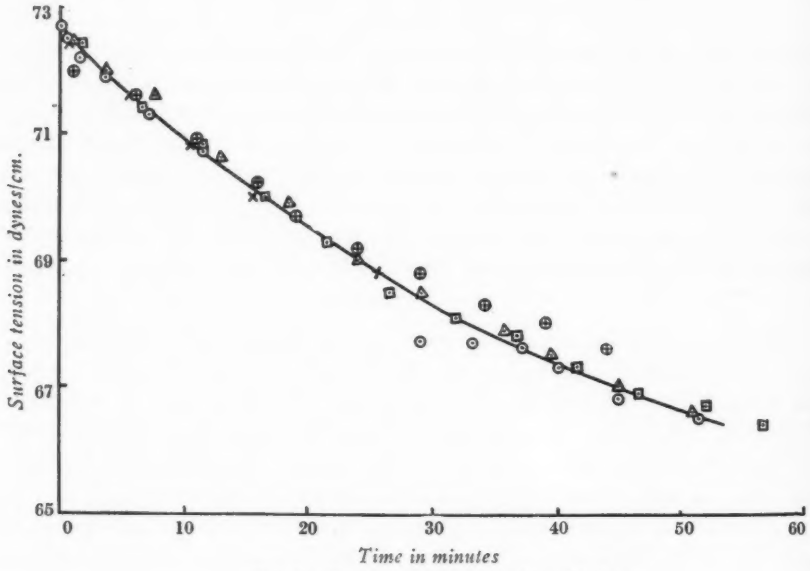


FIG. 1. Decrease of surface tension with time.

Increase in surface tension with time of an overcrowded surface.—It was found that a freshly formed surface of the 0·002 molar solution of benzopurpurin quickly developed a surface film as indicated by the development of a high surface pressure on movement of the barrier towards the float. It could be shown that the film was not caused by any accidental contamination ; for, repeated clearing by barriers did not eliminate the effect. With distilled water or amyl alcohol (in aqueous solution) this effect could not be detected. This showed that the film was formed by the accumulation of the benzopurpurin molecules at the surface. Certain other observations discussed later in the paper, have confirmed the view.

A surface which had aged for a few minutes could be overcrowded with the dyestuff molecules by the simple expedient of pushing the barrier towards

the float. The overcrowded surface exhibited an increase of surface tension with time. Some of the values obtained are indicated in Fig. 2.

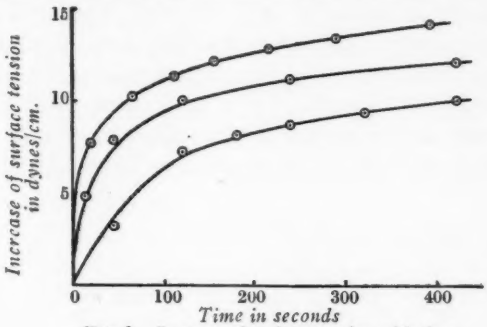


FIG. 2. Increase of surface tension with time.

The rate of accumulation of solute molecules and its temperature coefficient.—A few measurements of semi-quantitative character have been made on the rate of accumulation. It was felt that the accumulation in a 0·002 molar solution was rather too quick. A 0·0002 molar solution was therefore employed. In this solution, the variation of surface tension with time was extremely slow, the fall being about 0·4 dyne per cm. per hour. On the other hand, the formation of the surface film was appreciably fast. The surface pressure-area relations of a surface five minutes old were next investigated. For this purpose, the surfaces on either side of the float were cleared; the float was adjusted to zero position and the reading on the torsion head was noted. Then the torsion head was turned by 10°. To bring back the float to the zero position, it would be necessary to increase the surface pressure on one of the sides of the float to two dynes per centimetre, as each degree on the torsion balance corresponded to 0·2 dyne per cm. Exactly five minutes after clearing, the barrier on the appropriate side was carefully pushed so as to bring back the float to zero position. The final position of the barrier was read off on a scale, as also the position of the float. With these data the area corresponding to a surface pressure of two dynes per centimetre could be calculated. Similar determinations were made for different surface pressures starting with the barrier in the same initial position. The results are given in a former communication.[3]

The film appears to be more or less of the condensed type. The molecules strongly resist further compression when the surface is so crowded as to give a surface pressure of two dynes per centimetre. The dyestuff molecules seem to be closely packed at this stage.

The following technique was employed in studying the rate of accumulation. As before, the surfaces were swept and allowed to age for a definite

time. Knowing the distance between the barriers and the float and the width of the trough, the area of the ageing surface could be calculated. The torsion head was turned through 10°. At the appropriate time, the barrier was progressively moved towards the float until the latter just moved to the zero position. The final area between the barrier and the float was then noted. The ratio of the final to the initial area gave the fraction of the total surface covered by the solute molecules for that period of ageing. The time-area relations are given in Table II and Fig. 3.

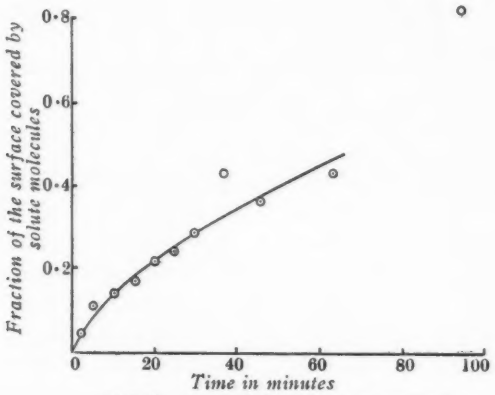


FIG. 3. Accumulation of solute molecules.

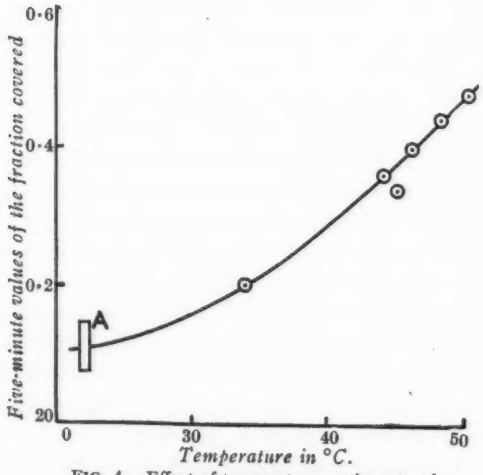


FIG. 4. Effect of temperature on the rate of accumulation.

It is seen from the graph (Fig. 3) that the time-area curves are not reproducible beyond twenty minutes. Investigations are being conducted to account for the poor reproducibility noted above. However, when the period of ageing is five minutes the values are fairly reproducible. Fig. 4 contains a rectangle A, which encompasses all the points representing some forty-seven independent determinations of the five-minute values made at about 22° C. The rate of accumulation is very much increased by a rise in temperature. The five-minute values obtained at higher temperatures are included in Table III, Fig. 4.

The maximum surface pressure developed on compression.—The maximum surface pressure that can be developed on an aged surface by pushing the barrier towards the float was determined. It was found to be approximately 54 dynes per cm.

Discussion.

Several explanations have been put forward for the variation of surface tension with time. Donnan and Barker[4] have assumed that " The variation is probably due to the high molecular weight and consequent slow rate of diffusion causing a relatively considerable time to be required for the establishment of the surface concentration at the fresh air and water surface." Milner[5] suggests that " The surface excess is so large that in dilute solutions the diffusion of sufficient oleate into the surface to form it takes an appreciable time." Ghosh and co-workers[6,7] have suggested two hypotheses. They assume that dyestuffs are polymerised when in solution. The polymers are supposed to be in equilibrium with the simple molecules. In their first hypothesis[6] they suggest that the polymers are preferentially adsorbed at the interface. Such preferential adsorption is accomplished by the movement of polymers from the bulk solution on to the surface. By making these assumptions and by considering the adsorption film to be gaseous in character they derive a formula to account for the experimental results. They have further interpreted the results of further work done by them on the basis of a new hypothesis[7] in which they assume that the simple molecules are preferentially adsorbed and these molecules are supplied by the bulk liquid but are not obtained by any depolymerisation at the surface. Lottermoser[8] has shown that the variations in the case of soap solutions are caused by the absorption of atmospheric carbon dioxide.

The following considerations show that the accumulation of solute molecules (noticed in the present investigation) is a *very slow* process. It has been found that the fraction of the area which gets covered by solute molecules in five minutes is 0·113 (average of about fifty values). Assuming that the cross-section of the molecules is of the order of 10^{-14} sq. cm., the

number of molecules which collect in five minutes works out to be $1 \cdot 13 \times 10^{13}$ per square centimetre. The rate of accumulation when the whole of the surface is bare would not be very different from this value as only one-tenth of the surface is covered in five minutes. The frequency of collisions of the solute molecules with the surface can be calculated[9] by the equation $Z = n\sqrt{\frac{RT}{2\pi M}}$ where Z is the collision frequency, n, the number of molecules of solute per c.c., R the gas constant per mole, T the absolute temperature and M the molecular weight of the solute. On calculating for 0·0002 M solution of benzopurpurin the collision frequency is found to be $2 \cdot 8 \times 10^{20}$ per second or $8 \cdot 4 \times 10^{22}$ collisions in five minutes. It is seen that the observed rate of accumulation and the calculated collision frequency differ by a factor of $7 \cdot 5 \times 10^{9}$.

These calculations definitely point out that the hypotheses of Donnan and Barker and of Milner are not correct. Milner's views would necessitate the assumption of an adsorption layer several centimetres in thickness. Both the hypotheses put forward by Ghosh and his co-workers are unsatisfactory. Their first hypothesis[6] assumes that the adsorption film is gaseous. This is not always the case. In the case of benzopurpurin and brilliant green for instance, the films are of condensed type. The second hypothesis of Ghosh and co-workers[7] is based on certain arbitrary assumptions which have been indicated earlier in this paper. Furthermore, to account for —on the basis of this hypothesis—observed facts like the slow rate of accumulation, the high temperature coefficient of the process and the manifestation of surface pressure, more assumptions of an arbitrary nature would be needed. With regard to Lottermoser's work, we would state that our systems are akin to those studied by Adam,[1] which show a " mysterious " fall of surface tension with time ; whereas absorption of carbon dioxide and oxygen of the atmosphere may have some influence on the surface tension in particular cases, it cannot account for variations obtained in systems studied by Adam or those dealt with in this paper.

The slowness of accumulation can best be accounted for by postulating the existence of a potential barrier which is to be crossed by the solute molecules before adsorption can take place. In other words, the adsorption is of the activated type. Activated adsorption is a phenomenon well known in colloid chemistry. But, the known cases of activated adsorption are all complicated by one or more of the following disturbing factors :—

(*a*) Solution of the adsorbate in the adsorbent,[10,11,12]

(*b*) Activated surface flow,[13]

(*c*) Persorption,[14]

(*d*) Diffusion through intercrystallite spaces and Smekal cracks,[15]
(*e*) Increase of easily penetrable cracks with rise in temperature,[16]
(*f*) Gas displacement effects[17,18] and
(*g*) Irreversible chemical combination.[19]

The slow accumulation observed in the present investigation is, however, a case of activated adsorption uncomplicated by any of the factors indicated above. The term activated adsorption has been used rather loosely in literature. While this term should be restricted to the *process* of adsorption, it has occasionally been employed to denote the *state* (the chemical activity) *of the adsorption layer.*[20] The term *activated accumulation* has therefore been employed to denote the phenomenon discussed in this paper. The energy of activation† works out to be about 13,400 calories. The high temperature coefficient of the rate of accumulation cannot be interpreted in terms of a mere increase in the frequency of collisions at the interface. On the other hand, the hypothesis of activation is in accordance with the observed facts. On the basis of the simple equation, the activation energy (calculated from the temperature coefficient) works out to be about 8,500 calories. It is to be noted that these values are only rough.

Further evidence in support of the existence of a potential barrier is given by the fact that a surface pressure is exerted by the film. When the glass barrier is pushed towards the float, an overcrowding of the surface is produced. Under these circumstances, there is a thermodynamic necessity for some of the molecules to leave the surface. Very few molecules however leave the surface as they have to re-cross the potential barrier in order to get into solution. They, on the other hand, bombard the float and cause a surface pressure. The maximum pressure exerted by the molecules is of special interest. After the attainment of the maximum surface pressure, further pushing of the barrier enables the molecules rapidly to enter the bulk solution. A lower limit of the energy of activation can be calculated in the following way :

† The postulation of a potential barrier is a generalised expression of the conditions prevalent at the interface. The exact nature of the barrier needs exploration. The present author finds that the slowness in accumulation is usually observed with the solute molecules having both a hydrophilic and a hydrophobic group. Such a molecule on adsorption would project the hydrophobic group away from the liquid. The process of dehydration (which may have to precede adsorption of the molecule) of the hydrophobic group may be an activated process. Definite suggestions cannot be made at present regarding the number of degrees of freedom involved in the activation. Further experimental work is needed. The energy of activation is calculated employing the usual formula (for the case involving two quadratic terms). In these calculations, the polymerisation of the solute molecules has been overlooked.

Energy of activation

$$= \frac{\text{Maximum surface pressure in dynes/cm.}}{\text{Number of molecules per sq. cm.}}$$

$$= \frac{54 \times 6 \times 10^{23}}{10^{14}} \text{ ergs per mole.}$$

or 7800 cals. per mole.

The general forms of the potential energy curves at the liquid vapour interface may now be discussed. The possible forms are indicated in Figs. 5, 6 and 7. The behaviour of the benzopurpurin solutions is represented in Fig. 5. Fig. 6 indicates the behaviour of solutions which do not exhibit

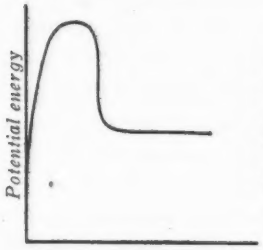


FIG. 5.

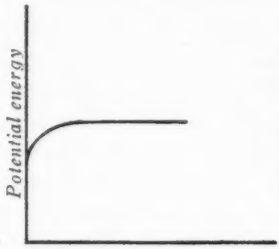


FIG. 6.

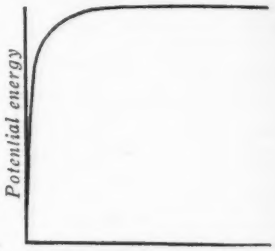


FIG. 7.

a variation of surface tension with time. Fig. 7 represents systems studied by Langmuir, Adam and others, namely, the films of insoluble substances. The distinction between the various classes does not appear to be sharp. For instance, nonylic acid in aqueous solution exhibits a finite, though small, energy of activation as has been found from measurements carried out in this laboratory.

Stability of Foams.

It is of interest to discuss the conditions under which a substance acts as a stabiliser of foam. To have a stable foam we must have a system in which the destruction of the interface can only be brought about by supplying a large amount of energy. The conditions that obtain in such a system can therefore be represented by Fig. 5. It has been experimentally observed that solutions exhibiting a variation of surface tension with time form stable foams. The surface pressure technique can therefore be used to measure the efficacy of a substance as a foam producer. It may be pointed out that for the production of stable foam an optimum energy of activation is needed. If the energy is too large, accumulation is so slow that the bubbles reunite before getting stabilised ; if the energy is too small, there is no stabilisation, as has already been pointed out. The energies of

activation of various foam producers are now being systematically studied in this laboratory.

The results set forth in this paper account for anomalous results met with in experimental work on Gibbs' adsorption equation. Substances that have been usually employed[21] for verifying this equation are those which produce stable foam and exhibit a variation of surface tension with time, (*e.g.*, sodium glycocholate, saponin, certain dyestuffs). In dilute solutions of these substances, the surface equilibrium is reached very slowly. Gibbs' equation cannot be expected to apply to such systems where equilibrium has not been attained. In more concentrated solutions, the equilibrium may be quickly attained. But in many of these cases a condensed solid film is formed at the surface so that it is doubtful whether the surface tension represents the free energy of the interface. Thus, the verification of

TABLE I.

The variation of surface tension with time of 0·002 *molar solution of benzopurpurin.*

Experiment 1		Experiment 2		Experiment 3		Experiment 4		Experiment 5	
Time	Surface tension	Time	Surface tension	Time	Surface tension	Time	Surface tension	Time	Surface tension
0′	72·7*	0′	72·7*	0′	72·7*	0′	72·7*	0′	72·7*
0·5′	72·5	1′	72·5	1·5′	72·4	1′	72·0	0·5′	72·4
1·5′	72·2	3·5′	72·0	6·5′	71·4	6′	71·6	5·5′	71·6
3·5′	71·9	7·5′	71·6	11·5′	70·9	11′	70·9	10·5′	70·8
7′	71·3	13·0′	70·6	16·5′	70·0	16′	70·2	15·5′	70·0
11·5′	70·7	18·5′	69·9	21·5′	69·3	19′	69·7	25·5′	68·8
29·0′	67·7	24·0′	69·0	26·5′	68·5	24′	69·2		
33·0′	67·7	29·0′	68·5	31·5′	68·1	29′	68·8		
37·0′	67·6	35·5′	67·9	36·5′	67·8	34′	68·3		
40·0′	67·3	39·5′	67·5	41·5′	67·3	39′	68·0		
45·0′	66·8	45·0′	67·0	46·5′	66·9	44′	67·6		
51·5′	66·5	51·0′	66·6	52·0′	66·7				
				56·5′	66·4				

* The surface tension of a freshly formed surface is assumed to be 72.7 dynes per cm.

TABLE II.

Time	Fraction covered by solute molecules
2′	0·051
5′	0·113
10′	0·139
15′	0·171
20′	0·218
25′	0·240
30′	0·286
37′	0·429
46′	0·362
63′	0·429
94′	0·819

TABLE III.

Temperature	Five-minute values of fraction covered by solute molecules
22°	0·113
34°	0·199
44°	0·362
45°	0·339
46°	0·398
48°	0·444
50°	0·480

Gibbs' equation cannot be rigorously made with such substances. Using nonylic acid Donnan and Barker[4] obtained satisfactory results. This can be accounted for by the small activation energy of the acid as has been found by experimental work using the present technique.

Several new lines of investigation suggest themselves in connection with the ageing of surfaces and are being undertaken in the laboratory. The effect of foreign substances on the energy of activation is of great interest. Preliminary experiments have shown that the activation energy is lowered by dissolved electrolytes. This is in accordance with the observation of Adam that salts accelerate the fall of surface tension with time.[1] A study of substances having small activation energies is also of importance. The application of this technique to the study of colloidal systems is likely to give valuable results. Application to liquid–liquid interfaces is of special interest from the point of view of the stability of emulsions. The technique, however, has to be suitably modified.

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stages of the investigation and his help in the preparation of this paper for publication.

Summary.

A new application of the Langmuir-Adam surface pressure technique has been made in the study of ageing of surface of solutions. It is found that a fresh surface of a solution of benzopurpurin exhibits a fall of surface tension with time. If by suitable methods, an overcrowding (by solute molecules) of the surface is brought about, such a surface exhibits a rise of surface tension in time. The molecules accumulated at the surface are shown to exhibit a reluctance to get into solution ; it has therefore been possible to measure the rate of accumulation and has been found to be very slow. The slowness is best accounted for on the basis of activated accumulation. The postulation of activation is further helpful in understanding (*a*) the time variation of surface tension, (*b*) the high temperature coefficient and (*c*) the manifestation of surface pressure. The results of the present investigation are extremely helpful in measuring the efficacy of a substance as the stabiliser of foam. Several new lines of investigation which have opened up are briefly indicated.

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DIELECTRIC COEFFICIENTS OF GASES AND VAPOURS.

Substituted Methanes and Ethane, Cyclopropane, Ethylene Oxide and Benzene.

By K. L. Ramaswamy.

(From the Departments of General Chemistry and Physics, Indian Institute of Science, Bangalore.)

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In a series of papers[1] dealing with the subject of dielectric coefficients, results of measurements on most of the stable gases have been recorded. Similar investigations have now been made on a number of organic substances in the gaseous condition and the results obtained form the subject of the present communication. Simultaneous determinations of the refractive indices and dispersions of the same specimens of materials were also made with a view to compare the results of dielectric coefficients with those of refractive indices at long wave-lengths, an account of which will be given in a separate paper.

Owing to the extraordinary difficulties in the purification of organic vapours, particularly of those which are liquids at the ordinary temperature, most of the earlier investigators have measured the dipole moments in the solution state. It has been often remarked that the values of polarisations obtained by extrapolation to infinite dilution do not represent the actual values in the free gaseous state. If very accurate values in the vapour state are desired, an accurate knowledge of either density or compressibility is essential. All earlier investigations show that in many cases the experimental errors are far greater than the corrections due to compressibility. It was considered therefore of extreme interest to make a systematic investigation using carefully purified specimens of materials. In this communication results of measurements on methyl fluoride, methyl and ethyl chlorides, methyl bromide, methyl iodide, carbon tetrachloride, chloroform, methylene chloride, acetone, acetonitrile, methyl alcohol, cyclopropane, ethylene oxide and benzene have been given.

[1] H. E. Watson, G. G. Rao and K. L. Ramaswamy, *Proc. Roy. Soc.*, A, 1931, **132**, 569; *ibid.*, 1934, **143**, 558; H. E. Watson and K. L. Ramaswamy, *ibid.*, 1936 (under publication); H. E. Watson, G. P. Kane and K. L. Ramaswamy, *ibid.*, 1936 (under publication); K. L. Ramaswamy, *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 364.

Of these, carbon tetrachloride, cyclopropane and benzene are definitely nonpolar. All other vapours have appreciable electric moments.

Experimental.

The apparatus, method of measurement and experimental procedure were in essence the same as described in the earlier papers.[2] Slight modifications had to be made for introducing the vapours of substances which are liquids at the ordinary temperature.

Measurements were made only at two temperatures, *viz.*, the temperature of the room and that of the steam. Only in the case of methyl fluoride the temperature of solid carbon dioxide also was employed. As in the earlier investigations,[2] the dielectric coefficient of carbon dioxide at different temperatures was determined at the beginning and at the end of the series of measurements. It was found that there was practically no change in the two sets of measurements made, showing that the calibrations of the condensers had not changed in the interval. The corrected mean values of $E-1^{760mm.}_{25^\circ} \times 10^6$ at 25° C. and 95° C. were respectively 901 and 902.

In the case of substances which are gaseous at the ordinary temperature, the purification was effected by the usual method of fractional distillation at low vapour pressures. The middle fractions boiling at constant vapour pressure were taken for the measurement. In every case identity of refractive index was taken as the criterion of purity.

For substances, which are liquids at the ordinary temperature and pressure, the purification was done as follows. The liquids were first carefully treated with suitable reagents when necessary and then distilled in an all-glass apparatus over drying agents like calcium chloride or phosphorous pentoxide. A small quantity of the purified material was then introduced into a bulb provided with a stem ending in a tap and having a side tube. The side tube was connected to a hyvac cenco pump with the necessary traps and the liquid allowed to boil. When all the dissolved air and more than half the bulk of the liquid were distilled, the material was condensed with a solid carbon dioxide bath and the side tube sealed off. The tube was afterwards joined to the main apparatus through a drying tube and the whole apparatus was completely evacuated. The tap was opened and the requisite amount of vapour allowed into one of the tubes of the interferometer and the refractive index balanced against air in the other tube. The vapour was next removed by condensation in another part of the apparatus which could be disconnected by closing a tap and a fresh quantity

[2] *Loc. cit.*

of the vapour again introduced. The process was repeated until two successive fractions agreed in refractive index. The necessary amount of material was then vapourised and fractionated if necessary and used for the measurements. Care was always taken to keep the pressure of the vapour far below the actual vapour pressure at the prevailing temperature of the room. A few measurements made in the beginning of this series using pressures near the saturation pressures indicated that the effects of adsorption were considerable and often gave very unreliable results. Later measurements at lower pressures, however, gave fairly consistent readings except in the case of one or two substances, which will be mentioned later.

It is necessary to mention that in the case of the vapours of high boiling liquids, the compresibilities could not be very accurately determined owing to the low pressures employed. In many cases, it was found rather unimportant as the experimental errors were often greater than the corrections due to compressibilities. However, as careful measurements as possible were made of the variations of refractive index with pressure at the ordinary temperature and the approximate values of compressibilities computed therefrom. At steam temperature, the values could not be directly determined and thus have been assumed to be one-third of those at the ordinary temperature.

Preparation of Materials.

Carbon tetrachloride, chloroform, methylene chloride, acetone, acetonitrile, methyl alcohol, methyl iodide, methyl amine and benzene were specimens from Kahlbaum, E. de Haën or Merck. The other gaseous substances were supplied by the Ohio Manufacturing Company in steel cylinders. Methyl fluoride and methyl bromide were prepared as given below.

The purity of the liquids was determined by their boiling points, densities and the values of refractive indices. The densities at different temperatures were measured with a pyknometer of the type recommended by Dr. H. E. Watson and employed by Govinda Rau and Narayanaswamy.[3] The refractive indices of the liquids were measured for two wave-lengths 5462Å and 4359Å with a Pulfrich refractometer.

Methyl fluoride was prepared by heating pure dimethyl sulphate with pure dry potassium fluoride. The gas was condensed at liquid air temperature and the incondensible impurity pumped off. It was then separated into ten fractions at −117°C. using solid ether at which temperature the vapour pressure was 49·2 mm. The fractionation was repeated twice. The refractive indices of the second and the seventh fractions were

[3] M. A. Govinda Rau and B. N. Narayanaswamy, *Zeit. Physikal. Chem.*, B, 1934, **26**, 23-44.

identical. These were then mixed and a small quantity of the light and heavy fractions were removed and the middle fractions employed for the purpose. In this connection my best thanks are due to Mr. K. Ganapathi for supplying me with a pure specimen of dimethyl sulphate.

Methyl chloride was labelled 99·5 per cent. pure. 250 c.c. of the gas when condensed at liquid air temperature, were found to contain about 6 c.c. of an incondensible fraction. This was removed and the gas collected into seven fractions at a constant vapour pressure of 90 mm. The condensible impurity when warmed to room temperature measured about 0·2 c.c. The gas was recondensed and fractionated as before. The middle fractions agreeing in refractive index were mixed and used in the measurements.

Methyl bromide was prepared by heating a mixture of pure methyl alcohol, sodium bromide and sulphuric acid. The gas was condensed at solid carbon dioxide temperature, at which temperature the vapour pressure was 5 mm., and a large quantity of the lighter fraction pumped off. It was then twice fractionated at a vapour pressure of 15 mm. into ten fractions. The middle fractions 3, 4, 5 and 6 agreeing in refractive index were mixed and used.

Methyl iodide was supplied by the preparation section of the Department of Organic Chemistry, Institute of Science. It was redistilled twice and the fraction boiling at 39°·0 ± 1°·0 C. at 680 mm. pressure was collected and used for the measurements. The density at 28°·2 C. was 2·252 grams per c.c. The refractive index for $\lambda = 5462$Å at the same temperature was 1·52937.

Ethyl chloride was labelled 99·5 per cent. pure. The gas appeared to be fairly pure. It was fractionated at a constant vapour pressure of 45 mm. Fractions 2, 3 and 4 agreeing in refractive index were mixed and employed in the measurements.

Methylene chloride from E. de Haën was first treated with concentrated sulphuric acid to remove the unsaturated compounds. The excess of the acid was neutralised with sodium carbonate, and the product washed with distilled water a number of times. Most of the water was removed by using a separating funnel. The product was then dried and distilled first over calcium chloride and then over phosphorous pentoxide. The middle fraction boiling at 42°·0 ± 0°·5 C. at 680 mm. pressure was used for the measurements. The density of the liquid at 23°·4 C. was 1·3612 grams per c.c. and the refractive indices at the same temperature for $\lambda = 5462$Å and $\lambda = 4359$Å were 1·43239 and 1·44089.

Chloroform.—E. de Haën's pure specimen was taken and treated similar to methylene chloride. The middle fraction boiling at 58°·2 ± 0°·1 C. at 680 mm. pressure was employed for the measurements. The density of the liquid at 24°·8 C. was 1·4802 grams per c.c. and the refractive indices at the same temperature for $\lambda = 5462$Å and $\lambda = 4359$Å were 1·44563 and 1·45451 respectively.

Carbon tetrachloride.—Merck's pure specimen free from carbon disulphide was however first refluxed over mercury for about twelve hours, and subsequently treated with concentrated sulphuric acid and sodium carbonate as in the case of methylene chloride and chloroform. After thorough washing with distilled water, the liquid was dried and distilled twice over phosphorous pentoxide. Middle fraction boiling at 73°·3 ± 0°·1 C. at 680 mm. pressure had a density of 1·5846 grams per c.c. at 25°·04 C. The values of refractive indices at the same temperature were 1·45963 and 1·46933 for $\lambda = 5462$Å and $\lambda = 4359$Å respectively.

Methyl alcohol used was a specimen from Kahlbaum certified to be free from acetone. It was, however, treated with sodium bisulphite, refluxed and finally distilled first over calcium chloride and later over metallic calcium. At 680 mm. pressure the boiling point was 61°·9 ± 0°·1 C. The density at 22°·72 C. was 0·7892 grams per c.c. and the refractive indices for the green and violet lines of mercury were respectively 1·32909 and 1·33463.

Acetone.—Kahlbaum's analytical reagent was refluxed over calcium chloride and distilled. The middle fraction boiling at 53°·2 ± 0°·1 C. at 680 mm. pressure was taken. At 22°·7 C. the liquid had a density of 0·7881 grams per c.c. and the refractive indices for the green and violet lines at the same temperature were 1·35911 and 1·36603.

Acetonitrile.—Kahlbaum's pure specimen was dried and distilled first over calcium chloride and then over phosphorous pentoxide. The boiling point of the middle fraction was 78°·0 ± 0°·2 C. at 680 mm. pressure. The density at 22°·8 C. was 0·7795 grams per c.c. and the refractive indices at the same temperature were 1·34582 and 1·35160 for the mercury green and violet lines.

Dimethyl ether was labelled 99·95 per cent. pure. When condensed at liquid air temperature, it was found to contain practically no incondensible impurity. The temperature was raised and the gas then collected at 60 mm. vapour pressure into seven fractions. A trace of condensible impurity was rejected. The fractionation was repeated and the middle fractions 2, 3 and 4 boiling at constant vapour pressure and agreeing in refractive index, were mixed and used in the measurements.

Methyl amine.—E. de Haën's pure and anhydrous specimen supplied in a sealed tube, was carefully opened in vacuum after cooling the bulb in solid carbon dioxide bath. About half a c.c. of the liquid was vapourised and passed through potassium hydroxide and then condensed. A large quantity of incondensible impurity at liquid air and solid carbon dioxide temperatures was rejected. It was then distilled at 25 mm. vapour pressure into ten fractions. The condensible impurity was separately removed. The gas was subsequently twice fractionated at a constant vapour pressure of 20 mm. and the middle fractions 3, 4, 5 and 6 agreeing in refractive index were mixed and employed for the measurements.

Cyclopropane was labelled 99·5 per cent. pure. About 200 c.c. of the gas when condensed at liquid air temperature contained 25 c.c. of an incondensible fraction probably air and hydrogen. The impurity was removed. The solid was then evaporated and condensed in quick succession and the traces of incondensible impurity present were pumped off simultaneously. The fractions 2 to 6 were collected at a constant vapour pressure of 42 mm. A little heavy fraction present was rejected. It was again distilled at 45 mm.vapour pressure into tubes and the middle fractions 3, 4 and 5 agreeing in refractive index were mixed, refractionated and used in the measurements.

Ethylene oxide.—The purity of the compound was not given by the manufacturers. There appeared to be no incondensible impurity at liquid air temperature. The vapour pressure was 2 mm. at solid carbon dioxide temperature. The gas was distilled at 15 mm. steady vapour pressure into 5 fractions. The condensible impurity when warmed to room temperature had a vapour pressure of 20 mm. and when opened to phosphorous pentoxide, the pressure went to zero millimetres indicating that the impurity was probably water. The fractions 2, 3 and 4 agreeing very nearly in refractive index, were mixed, refractionated and used for the measurements.

Benzene.—Kahlbaum's molecular weight benzene, free from thiophene, was refluxed and distilled twice over phosphorous pentoxide. The liquid boiled at 78°·2 ± 0°·2 C. at 680 mm. pressure and had a density of 0·8747 grams per c.c. at 23°·05 C., at which temperature the refractive indices for the mercury green and violet lines were respectively 1·50445 and 1·52211.

Results.

Owing to the small pressures employed in the case of substances which are liquids at the ordinary temperature and pressure, the same accuracy as in the case of the gases could not be obtained. Attempts were made to read the pressures more accurately using a micrometer eye-piece instead

of the simple telescope actually employed in other measurements. But the corrections due to large meniscus heights and high values of compressibilities which could not be determined to the same degree of accuracy, were considerable. In some cases, the capacities measured were rather small to permit of greater accuracy.

In Table I are given the results of measurements. All values in which either the oscillators appeared unsteady or in which the purity of the material was somewhat doubtful have been omitted. Only those which were sufficiently satisfactory have been given. Each value is usually the mean of five or six readings. Column 1 gives the serial number of the experiment. Columns 2, 3, 4 and 5 give respectively the temperature θ_g in degrees Centigrade, the actual corrected pressure difference dp, the mean pressure P_m, and the number of individual readings in an experiment. The 6th column gives the values of $\dot{E}-1$ calculated to 760 mm. pressure and 25°·0 C. on the assumption that the gas or vapour obeys the ideal gas laws. In the 7th column are given the final values of $\dot{E}-1$ at 760 mm. pressure and 25°·0 C. corrected for compressibility. Any subsequent treatments given to the substance and other particulars are mentioned in the last column. In the case of substances which are liquids at the ordinary temperature and pressure, the values at 760 mm. and 25°·0 C. appear meaningless since they cannot exist as vapour under those conditions. They must only be taken to represent what they would be if they could be measured at 760 mm. and 25°·0 C.

TABLE I. *Values of E-1 reduced to 760 mm. pressure and 25° ·0 C.*

No.	θ_g°C.	*dp* in mm.	P_m	No. of readings	E — 1	$E-1_{p=0}$	Remarks
			1. Methyl fluoride.				
1	26·4	178·95	114	5	·009464	·009436	Dispersion measured.
2*a*	,,	88·75	160	,,	·009499	·009459	
b	,,	90·20	69·5	,,	·009449	·009432	
3*a*	*95·0*	256·25	161·5	,,	*·007843*	*·007832*	Trace of incondensible removed.
b	*95·2*	256·50	,,	,,	*·007841*	*·007830*	
c	,,	256·65	,,	,,	*·007836*	*·007825*	
4	27·1	184·25	117	,,	·009440	·009411	
5*a*	27·2	90·60	164·5	,,	·009468	·009428	
b	,,	93·65	72	,,	·009446	·009428	
6	*−79·8*	85·25	56·8	,,	*·014225*	*·014146*	
7*a*	,,	35·15	82·3	,,	*·014255*	*·014141*	
b	,,	50·15	39·2	,,	*·014235*	*·014181*	
8	,,	85·30	56·8	,,	*·014235*	*·014156*	
9	,,	46·90	31·0	,,	*·014215*	*·014172*	
10	,,	82·60	54·9	,,	*·014215*	*·014139*	
11	27·7	180·30	115·1	,,	·009430	·009402	Gas refractionated.
12	27·9	179·65	114·7	4	·009430	·009402	
13	*95·4*	248·90	156·9	5	*·007840*	*·007829*	No incondensible fraction.
14	,,	248·15	156·4	,,	*·007831*	*·007820*	
15*a*	*−79·8*	88·72	160·3	6	*·014364*	*·014140*	
b	,,	84·75	72·9	,,	*·014245*	*·014144*	
16	,,	84·62	56·7	5	*·014235*	*·014156*	

TABLE I.—(*Contd*).

No.	θ_g°C.	*dp* in mm.	P_m	No. of readings	E — 1	E — $1_{p=0}$	Remarks
				2. Methyl Chloride.			
1	24·1	150·55	95	5	·010520	·010470	Dispersion measured.
2*a*	24·0	73·95	134	,,	·010570	·010500	No incondensible fraction.
b	,,	76·65	58	,,	·010500	·010470	
c	,,	150·65	95	,,	·010530	·010480	
3	,,	150·70	,,	4	·010520	·010470	
4	*95·2*	170·35	106	5	*·008626*	*·008612*	
5	,,	170·70	,,	,,	*·008616*	*·008602*	
6	,,	170·75	,,	,,	*·008614*	*·008600*	
7	,,	99·80	61	,,	*·008596*	*·008588*	Some gas removed.
8	22·2	150·30	96	,,	·010570	·010520	Next day. Refractionated.
9*a*	,,	74·05	134	6	·010620	·010550	Disp. remeasured.
b	,,	76·10	59	,,	·010570	·010540	
10	,,	150·10	96	7	·010590	·010540	
11	*95·3*	166·20	104	5	*·008719*	*·008705*	No incondensible fraction.
12	*95·4*	166·00	,,	,,	*·008719*	*·008705*	
13	,,	89·85	56	6	*·008709*	*·008701*	
				3. Methyl bromide.			
1	23·0	155·10	99	5	·010120	·010050	
2*a*	23·1	77·80	138	6	·010190	·010100	
b	,,	77·40	60	,,	·010100	·010060	
3	23·2	155·35	99	5	·010130	·010060	No incondensible fraction.
4	*95·0*	173·50	109	,,	*·008429*	*·008409*	

TABLE I.—(*Contd.*).

No.	θ_g°C.	*dp* in mm.	P_m	No. of readings	E — 1	$E-1_{p=0}$	Remarks
			3. Methyl bromide.—(contd.)				
5	*95·0*	173·60	109	5	*·008421*	*·008401*	
6	,,	,,	,,	,,	*·008406*	*·008386*	
7	24·1	154·95	99	,,	·010080	·010020	Disp. measured.
8	,,	154·90	,,	,,	·010090	·010030	No incondensible fraction.
9	*95·4*	172·35	108	5	*·008444*	*·008424*	
10	,,	172·30	,,	6	*·008444*	*·008424*	
			4. Methyl iodide.				
1	28·2	110·25	70	5	·009034	·008956	Disp. measured.
2	,,	109·70	69·7	,,	·009032	·008954	Trace of incondensible removed.
3	,,	109·45	69·5	,,	·009025	·008947	
4	*95·4*	123·00	76·8	,,	*·007773*	*·007748*	No incondensible present.
5	,,	122·05	76·3	4	*·007773*	*·007749*	
6	,,	121·65	76·0	5	*·007757*	*·007733*	
7	,,	121·25	75·7	,,	*·007741*	*·007717*	
			5. Ethyl chloride.				
1	22·6	116·20	73	5	·013030	·012950	Disp. measured.
2*a*	22·5	54·50	105	,,	·013020	·012910	No incondensible fraction.
b	,,	61·85	46	,,	·013020	·012970	
3	,,	116·35	74	,,	·013020	·012940	
4	22·4	116·40	,,	,,	·012990	·012910	
5	*95·2*	132·60	82	,,	*·010730*	*·010710*	

TABLE I.—(*Contd.*).

No.	θ_g°C.	*dp* in mm.	P_m	No. of readings	E − 1	E − $1_{p=0}$	Remarks
			5. Ethyl chloride.—(contd.)				
6	*95·2*	132·70	82	5	*·010740*	*·010720*	
7	*95·3*	,,	,,	,,	*·010730*	*·010710*	
8	23·0	117·00	74	4	·012890	·012810	Next day.
9*a*	,,	53·60	105	,,	·013020	·012910	Trace of incondensible removed.
b	,,	62·40	46	,,	·013010	·012960	
10	*95·2*	130·40	81	5	*·010800*	*·010780*	
11	,,	130·30	80	,,	*·010800*	*·010780*	
			6. Methylene chloride.				
1	24·2	99·90	63	11	·008340	·008250	Disp. measured.
2	,,	40·65	32	7	·008350	·008304	
3	,,	95·90	61	6	·008362	·008275	
4	*95·5*	107·30	67	7	*·007132*	*·007105*	No incondensible fraction.
5	,,	41·75	33	6	*·007169*	*·007156*	
6	*95·5*	72·80	45	,,	*·007147*	*·007129*	
7	23·8	84·95	54	8	·008345	·008268	Disp. repeated next day.
8	,,	34·40	27	6	·008387	·008349	No incondensible fraction.
9	*95·2*	95·35	59	,,	*·007126*	*·007102*	
10	,,	36·75	29	7	*·007173*	*·007161*	
11	*95·3*	90·30	56	,,	*·007126*	*·007104*	

TABLE I.—(*Contd.*).

No.	θ_g°C.	*dp* in mm.	P_m	No. of readings	E − 1	$E-1_{p=0}$	Remarks
				7. Chloroform.			
A 1	24·8	132·60	86	9	·005714	·005590	Untreated with H_2So_4, etc.
2	*95·2*	143·50	91	7	*·005097*	*·005058*	Disp. measured.
3	,,	143·50	,,	,,	*·005110*	*·005071*	
4	,,	141·65	90	6	*·005141*	*·005102*	
5	25·3	131·45	85	10	·005667	·005545	Next day.
6	*95·1*	144·35	92	6	*·005097*	*·005057*	
7	,,	,,	91	8	*·005114*	*·005075*	
8	25·1	129·35	84	4	·005663	·005543	Next day. No incondensible fraction.
9	,,	,,	,,	6	·005673	·005553	
B 10	24·5	126·00	82	5	·005831	·005710	Treated with H_2So_4, etc.
11	24·6	126·85	83	8	·005820	·005698	Disp. repeated.
12	24·8	77·35	49	9	·005840	·005767	
13	,,	32·60	26	5	·005734	·005696	
14	*95·4*	35·65	28	7	*·005193*	*·005181*	
15	*95·3*	36·50	,,	6	*·005187*	*·005175*	
16	*95·2*	78·95	50	,,	*·005248*	*·005226*	
17	24·6	69·80	44	8	·005798	·005734	No incondensible fraction.
18	,,	57·50	37	7	·005795	·005741	
19	,,	29·75	24	6	·005787	·005752	
20	*95·2*	78·10	49	8	*·005273*	*·005251*	
21	,,	31·60	25	4	*·005211*	*·005200*	

TABLE I.—(*Contd.*).

No.	θ_g°C.	*dp* in mm.	P_m	No. of readings	E − 1	$E - 1_{p=0}$	Remarks
			8. Carbon tetrachloride.				
1	24·4	79·70	52	11	·003558	·003489	Disp. measured.
3	30·2	75·35	49	3	·003542	·003477	Next day.
4	28·2	73·45	47	11	·003536	·003474	
6	*95·4*	79·45	50	8	*·003554*	*·003532*	
5	,,	78·50	49	7	*·003583*	*·003561*	
7	*95·3*	81·65	50	,,	*·003569*	*·003547*	
8	*95·0*	81·00	51	,,	*·003584*	*·003561*	
9	28·2	72·35	46	6	·003588	·003527	Next day. Trace of incondensible fraction removed.
10	28·2	72·65	,,	,,	·003569	·003508	
11*a*	22·6	34·20	22	5	·003486	·003458	Different sample. Ref. index measured.
b	,,	34·20	,,	,,	·003480	·003452	
c	,,	33·25	,,	6	·003485	·003457	
12	*95·0*	38·90	24	3	*·003466*	*·003456*	
13*a*	,,	38·35	,,	5	*·003433*	*·003423*	No incondensible impurity.
b	,,	37·50	,,	6	*·003498*	*·003488*	
14	,,	36·90	28	4	*·003458*	*·003446*	
			9. Methyl alcohol.				
3	*95·0*	71·15	46	5	*·006940*	*·006927*	
4	*95·2*	70·20	,,	6	*·006935*	*·006922*	
5	,,	69·50	45	,,	*·006938*	*·006925*	
15	24·3	51·05	33	,,	·008675	·008640	Ref. index measured.

TABLE I.—(*Contd.*).

No.	θ_g°C.	*dp* in mm.	P_m	No. of readings	E — 1	E — $1_{p=0}$	Remarks
			9. Methyl alcohol.—(contd.)				
16	*95·1*	68·15	43	4	*·006867*	*·006855*	
17	,,	68·30	,,	5	*·006864*	*·006852*	
18	,,	67·95	,,	,,	*·006875*	*·006863*	
19	24·3	46·00	30	,,	·008792	·008759	Ref. index measured.
20	24·2	45·90	,,	,,	·008825	·008792	No incondensible fraction.
23	*95·3*	44·30	28	,,	*·006890*	*·006882*	
24	28·9	39·40	25·2	4	·008192	·008166	Measurements repeated.
25	28·9	39·40	25·2	,,	·008192	·008166	
26	28·8	39·85	25·5	5	·008138	·008112	
27	*95·4*	47·85	30·2	,,	*·006878*	*·006869*	
28	,,	47·55	30·0	4	*·006849*	*·006840*	
29	,,	47·45	,,	5	*·006862*	*·006853*	
			10. Acetone.				
1	23·6	66·50	42	5	·02354	·02313	
2	,,	66·60	,,	,,	·02353	·02312	
4	,,	66·70	,,	,,	·02351	·02310	Ref. index measured.
5	*95·2*	76·10	47	4	*·01884*	*·01872*	
6	,,	76·55	48	6	*·01882*	*·01870*	
7*a*	,,	38·55	67	5	*·01874*	*·01857*	
b	,,	38·40	29	,,	*·01877*	*·01870*	
8	,,	76·95	48	,,	*·01875*	*·01863*	
9	23·4	67·20	43	,,	·02342	·02301	Ref. index remeasured.
10	,,	66·90	,,	,,	·02344	·02303	No incondensible impurity.
11	*95·4*	76·90	48	,,	*·01888*	*·01876*	
12	*95·6*	,,	,,	6	*·01880*	*·01868*	

TABLE I—(*Contd.*).

No.	θ_g°C.	*dp* in mm.	P_m	No. of readings	E — 1	E — $1_{p=0}$	Remarks
			11. Acetonitrile.				
2	23·2	36·00	23	5	·03947	·03877	Disp. measured.
5	22·8	18·90	12	4	·03969	·03932	Trace of incondensible removed.
6	,,	19·00	,,	5	·03979	·03942	
7	*95·6*	36·00	22	,,	*·03164*	*·03146*	
9	28·4	31·55	20	,,	·03959	·03899	Different sample.
10	,,	31·50	,,	4	·03956	·03896	Disp. remeasured.
11	,,	31·55	,,	5	·03946	·03886	
12	,,	31·50	,,	,,	·03944	·03884	
13	*94·9*	34·55	21·5	,,	*·03157*	*·03140*	A bubble of incondensible removed.
14	*95·1*	34·65	,,	,,	*·03144*	*·03127*	
15	*95·1*	34·65	,,	6	*·03141*	*·03124*	
			12. Dimethyl ether.				
1	23·8	269·20	172	5	·006093	·006041	Ref. index measured.
2*a*	,,	128·90	243	,,	·006105	·006031	
b	,,	140·20	107	,,	·006068	·006036	
3	,,	268·90	171	4	·006086	·006034	
4	*95·2*	303·70	190	5	*·005237*	*·005221*	No incondensible fraction.
5	,,	,,	,,	,,	*·005237*	*·005221*	
6	,,	,,	,,	,,	*·005234*	*·005218*	
7*a*	23·5	267·60	173	,,	·006094	·006042	Refractionated.
b	,,	,,	,,	,,	·006088	·006036	
8*a*	*95·5*	301·70	192	6	*·005231*	*·005215*	
b	,,	301·60	,,	5	*·005236*	*·005220*	

TABLE I—(*Contd.*).

No.	θ_g°C.	*dp* in mm.	P_m	No. of readings	E — 1	$E - 1_{p=0}$	Remarks
				13. Methyl amine.			
1	24·0	143·60	92	5	·005804	·005763	Ref. index measured.
2	,,	141·30	90	,,	·005836	·005796	
3	*95·2*	170·90	107	,,	*·004719*	*·004706*	
4	,,	170·55	,,	,,	*·004704*	*·004691*	
5	,,	170·40	,,	,,	*·004703*	*·004690*	
6	24·8	123·80	79	,,	·005682	·005647	Refractionated gas.
7	,,	123·45	,,	,,	·005668	·005633	Ref. index remeasured.
8	*95·2*	137·95	86	,,	*·004882*	*·004871*	
9	,,	136·90	,,	4	*·004902*	*·004891*	
10	24·7	96·45	61	5	·005573	·005547	Next day.
11	,,	95·80	,,	6	·005581	·005555	
12	*95·2*	115·35	,,	5	*·004930*	*·004922*	
13	,,	115·10	,,	4	*·004940*	*·004932*	
14	*95·4*	115·05	,,	5	*·004924*	*·004916*	
				14. Cyclopropane.			
1	23·4	521·30	345	8	·001778	·001752	Disp. measured.
2	,,	513·70	342	5	·001774	·001748	
3	,,	513·60	,,	4	·001774	·001748	
4*a*	,,	257·80	472	5	·001785	·001749	
b	,,	255,·90	213	,,	·001771	·001755	
5	*95·1*	555·90	364	,,	*·001762*	*·001753*	

TABLE I—(*Contd.*).

No.	θ_g°C.	dp in mm.	P_m	No. of readings	E — 1	E — $1_{p=0}$	Remarks
			14. Cyclopropane.—(contd.)				
6	*95·1*	555·60	314	5	*·001762*	*·001753*	
7	*95·2*	555·50	,,	,,	*·001764*	*·001755*	
8	23·6	516·20	343	,,	·001775	·001749	Refractionated gas.
9	,,	,,	,,	,,	·001775	·001749	
10	*95·4*	554·70	362	,,	*·001761*	*·001752*	
11	*95·2*	554·50	,,	,,	*·001760*	*·001751*	
			15. Ethylene oxide.				
1	24·6	91·20	57	7	·010620	·010570	
2	23·6	161·75	103	4	·010700	·010610	Disp. measured.
3*a*	,,	80·90	144	5	·010770	·010645	
b	,,	81·10	62	,,	·010690	·010635	
4	,,	162·10	103	,,	·010690	·010600	
5	*95·3*	182·00	113	,,	*·008800*	*·008773*	No incondensible fraction.
6	,,	181·70	,,	,,	*·008804*	*·008777*	
7	,,	181·50	,,	,,	*·008798*	*·008771*	
8	24·7	163·70	104	,,	·010610	·010520	Next day.
9	24·8	161·20	102	,,	·010670	·010580	Refractionated.
10	,,	161·15	,,	,,	·010660	·010570	
11	*95·4*	180·20	112	,,	*·008819*	*·008792*	
12	,,	179·95	,,	,,	*·008815*	*·008788*	
13	,,	179·85	,,	,,	*·008813*	*·008786*	

TABLE I—(*Contd.*).

No.	θ_g°C.	*dp* in mm.	P_m	No. of readings	E — 1	$E - 1_{\rho=0}$	Remarks
				16. Benzene.			
1	24·8	33·55	22	5	·003400	·003348	Disp. measured.
2	24·6	33·60	,,	,,	·003422	·003370	
3	*95·3*	38·45	24	,,	*·003461*	*·003442*	
5	24·8	31·35	20	,,	·003436	·003389	Next day.
6	24·7	31·30	,,	,,	·003428	·003381	
7	*95·4*	31·80	,,	4	*·003409*	*·003393*	
8	,,	,,	,,	6	*·003480*	*·003464*	
9	,,	31·70	,,	4	*·003462*	*·003446*	
10	23·0	41·10	27	5	·003382	·003319	Fresh sample. Disp. repeated.
11	23·4	40·80	,,	,,	·003374	·003311	
12	,,	40·55	,,	4	·003382	·003319	
14	*95·1*	37·25	24	5	*·003334*	*·003316*	
15	,,	35·85	22	,,	*·003387*	*·003370*	

In Table II, the actual values of compressibilities obtained from measurements of refractive index are given. The figures represent the percentage corrections for a mean pressure of 380 mm. or for a change of pressure from 0 to 760 mm. In the case of substances which are liquids at the ordinary temperature and pressure, the values merely represent what they would be if measured at 760 mm. pressure and the compressibility were linear, which is not always true. In correcting the values of dielectric coefficients, it is assumed that the effect of adsorption on the condenser plates is not appreciably different from that on the plates of the interferometer.

The values were not in all cases determined at 25°C., but have been measured at the prevailing laboratory temperatures. In applying the corrections to the dielectric coefficient values, it has been assumed that the compressibilities would not vary considerably within small ranges of

temperature. As it was not possible to obtain the values at the steam temperature directly, it is assumed that a third of the values at the room temperature would not be far from correct.

The temperature and the mean pressure at which the measurements of refractive index were made have also been given.

TABLE II.

Percentage compressibility corrections.

Substance	Temp.° C.	Mean pressure	Comp. correction %	Remarks
Methyl fluoride ..	26·6	306	0·99	
,, ,, ..	*−79·8*		*3·7*	(d. k. measurement.)
,, chloride ..	22·6	309	1·81	Mean of 2 determinations.
,, bromide ..	23·6	333	2·51	
,, iodide ..	28·1	55	4·69	
Ethyl chloride ..	23·0	262	3·11	
Methylene chloride	25·0	78	6·5	Mean of 3 values.
Chloroform ..	25·0	72	9·6	Mean of 2 values.
Carbon tetrachloride	24·5	35	14·1	,, ,,
Methyl alcohol ..	23·6	35	4·7	,, ,,
Acetone ..	23·5	38	15·6	,, ,,
Acetonitrile ..	23·7	38	29·2	
Dimethyl ether ..	23·0	209	1·88	
Methyl amine ..	25·2	268	2·93	Mean of 2 values.
Cyclopropane ..	23·4	303	1·61	
Ethylene oxide ..	25·0	301	3·08	
Benzene ..	24·8	19	26·2	Mean of 2 values.

The individual values call for a little comment. *Methyl fluoride* gave steady and concordant values. Owing to the small pressure employed, the value of compressibility at solid carbon dioxide temperature could not

be determined with greater accuracy and the value given appears to be a little too high.

The early values of *methyl chloride* at the steam temperature are appreciably lower than those in experiments 11–13. The gas was refractionated in the interval and a small amount of incondensible impurity was removed. For the final calculations, values of experiments 8–13 have been preferred since the gas was decidedly purer than in the earlier experiments. The small deviations in the case of *methyl bromide* and *methyl iodide* are within the limits of experimental error. In the case of *methyl iodide* care was taken to complete the measurements as quickly as possible to avoid any possible decomposition.

The results of *ethyl chloride* and *methylene chloride* are sufficiently concordant and the deviations indicated are within the limits of experimental error. In the case of *chloroform* experiments were made with two different samples A and B, one of which was untreated with sulphuric acid and sodium carbonate and the other carefully purified as mentioned earlier. Results, though good enough among themselves, are different with different samples. The untreated sample gave a value for the moment of $0 \cdot 99 \times 10^{-18}$. The large variations in the values given are probably due to slow changes in the nature of the material. The mean values have been adopted as the most probable in the calculation of the moment.

The deviations in the values for *acetone* are within limits of experimental error and the individual readings were sufficiently concordant. The earlier values of *acetonitrile* are not so concordant as the later values 9–15. The latter measurements were made with greater care and quickness. The figures in experiments 9–15 have been taken in the calculation of the moment. With *methyl alcohol* the effects of adsorption appeared to be considerable. The values at the steam temperatures are fairly concordant and the earlier irregular and discordant values at the room temperature have been omitted. In the latter experiments 24–29 the purified *methyl alcohol* was treated with pure and dry potassium hydroxide pellets (alcohol-free). The values were more concordant and steady and these have been taken as more reliable in the calculation of the moment. It appears therefore that the earlier high values at the room teperature are probably due to the presence of unsaturated aldehydes, etc.

Dimethyl ether, *cyclopropane* and *ethylene oxide* gave fairly satisfactory results. But *methyl amine* gave at first results indicating a high moment. The gas had been kept for several months. On refractionation it appeared to give a better set of results. However, it was noticed that the gas was not

quite stable and underwent decomposition as could be seen from results in experiments 10–14. Results of experiments 6–9 which are the most probable have been employed in calculating the moment.

The results on *carbon tetrachloride* and *benzene* are not very concordant owing to the effects of adsorption and the small pressures employed. Errors in the measurements of small capacities also have contributed to the variations in the values. They however indicate that these compounds have practically no dipole moment.

Most of the substances mentioned have been investigated by previous workers and a comparison of the results is interesting. Owing to the different methods of representation of results and the varying temperatures and pressures at which the measurements have been made, it is often difficult to judge the merits of any particular series. In many cases, the details of measurement and of the purity of the materials employed are not available and measurements have been done at a single temperature. In no case, however, simultaneous determination of refractive index and dispersion appear to have been made on the same specimen of the substance.

In Table III (A) most of the available data in the gaseous state are shown calculated to 25°·0 C. and 760 mm. pressure. Table III (B) contains the results of the author and of G. Pohrt[4] who has given results for a number of substances at only one temperature. The author's values are all corrected for compressibility and have been obtained from the polarisations given in Table IV. With the exception of the values by Fuchs, the results by other authors do not appear to have been corrected for compressibility.

The figures in Table III (A) show that the results of different authors are not as concordant as one would expect. The difficulties in the purification of many substances mentioned in this paper are far greater than in the case of the more stable gases. In addition, the effects of adsorption on the condenser plates often may give rise to spurious results unless low pressures are employed. The results obtained, however, do in many cases agree with the more recently determined values by Fuchs, Zahn, Stuart, Miles and Kubo. The earlier values by Sänger are not in agreement with the author's but the later ones are practically in good agreement. It is satisfactory to note that the value of 331 for benzene obtained by Smyth and Mcalpine is very close to the figure 333 obtained by the author.

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[4] G. Pohrt, *Ann. Physik.*, 1913, **42**, 569.

TABLE III (A).

Values of $E-1 \times 10^5$ *at 760 mm. and 25°·0 C.*

Gas or Vapour	Author	Others*
Methyl fluoride ..	948	
„ chloride ..	1045	988 (S); 913 (Si); 1067 (S & St); 1184 (M); 1047 (F).
„ bromide ..	1001	1002 (M).
„ iodide ..	902	963 (M & S G); 899 (M).
Ethyl chloride ..	1286	1256 (Si); 1292 (S & St); 1261 (M); 1285 (F).
Methylene chloride ..	827	945 (S); 730 (M).
Chloroform A ..	555	578 (S); 553 (Si).
„ B ..	574	
Carbon tetrachloride..	345	350 (S).
Acetonitrile ..	3918	
Acetone ..	2297	2355 (Stu); 2333 (Stu); 2320 (Z).
Dimethyl ether ..	602	620 (Stu); 621 (S & St).
Methyl amine ..	564	554 (St); 384 (G & C).
„ alcohol ..	824	833 (Mi); 848 (K).
Ethylene oxide ..	1058	1076 (Stu).
Cyclopropane ..	175·2	
Benzene ..	333	331 (Sm & Mc).

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TABLE III (B).

Values of $E-1 \times 10^5$ *reduced to* 760 *mm. and* 25°·0 *C.*

Gas or Vapour	Temp. °C. (abs.)	Author	G. Pohrt
Methyl chloride ..	373·1	855	870
,, bromide ..	373·1	832	850
,, iodide ..	372·7	767	793
Ethyl chloride ..	373·1	1063	1059
Methyl alcohol ..	372·3	679	709
,, cyanide ..	373·0	3093	3304
,, amine ..	372·9	484	472
,, ether ..	372·5	518	517
Acetone ..	372·4	1851	1986
Benzene ..	373·1	334	345
Carbon dioxide ..	273·1	902	911

On looking at the results in Table III (B), it is clear that the values of the author are, in general, lower than those of Pohrt except for ethyl chloride and methyl ether which are slightly higher. The value by the author for methyl amine is distinctly higher than that of Pohrt.

In Table IV are given the values of polarisation, constants A and B and of dipole moments. Against each gas or vapour is mentioned in the first column the temperature in degrees Centigrade. The second column gives the polarisation calculated by multiplying $E-1/E+2$ by the number 24465 which represents the gram-molecular volume in cubic centimetres for an ideal gas at 760 mm. pressure and 25°·0 C. The values of the constants A and B are given in columns 3 and 4, the fifth column giving the electrical moments. In the final column are given the values of dipole moments obtained by other investigators in the gaseous condition.

TABLE IV.

Polarisation, A, B and μ.

Gas or Vapour	Temp. °C.	P	A	B	μ	μ by others†
Methyl fluoride ..	−79·8	114·85				
			7·32	20790	1·83	
	25·0	77·06				
			6·86	20920	1·84	
	95·2	63·67				
mean ..			7·09	20855	$1·83_5$	1·81 (Sm & Mc).
Methyl chloride ..	23·1	85·40				1·86 (S);
			8·66	22730	1·92	1·97 (S);
	95·3	70·35				1·69 (Si);
						1·85 (S & St);
						1·89 (Stu);
						2·002 (M);
						1·86 (F).
Methyl bromide ..	23·6	81·68				
			13·36	20280	1·81	1·786 (M).
	95·2	68·40				
Methyl iodide ..	28·2	72·78				
			18·65	16310	1·63	1·313 (M & S G);
	95·1	62·93				1·623 (M).
Ethyl chloride ..	22·7	105·05				
			15·21	26580	2·07	1·98 (Si);
	95·2	87·35				2·00 (S & St);
						2·08 (Stu)
						1·997 (M).
Methylene chloride	24·0	67·45				
			18·74	14470	1·53	1·59 (S);
	95·4	58·00				1·621 (M & S G).
Chloroform A ..	25·2	45·16				
			24·72	6096	0·99	
	95·1	41·27				0·95 (S);
						1·05 (Si).
B ..	24·6	46·72				
			24·92	6491	1·02	
	95·2	42·54				
Carbon tetrachloride	22·6	28·14				
			28·14	0	0	0 (S).
	95·0	28·14				

TABLE IV—(*Contd.*)

Gas or Vapour	Temp. °C.	P	A	B	μ	μ by others†
Methyl alcohol ..	28·9	66·27	8·14	17560	1·69	1·68 (Mi); 1·69 (K).
	95·4	55·77				
Acetone ..	23·5	186·8	6·0	53650	2·95	2·84 (Stu); 2·85 (Z).
	95·4	151·5				
Acetonitrile ..	25·0	315·6	−11·9	97660	3·98	
	95·2	253·1				
Dimethyl ether ..	23·6	49·14	15·03	10130	1·28	1·29 (Stu); 1·316 (S).
	95·5	42·48				
Methyl amine ..	24·8	45·91	13·65	9612	1·25	1·23 (St); 0·99 (G & C).
	95·2	39·74				
Cyclopropane ..	23·5	14·27	14·28	0	0	
	95·3	14·29				
Ethylene oxide ..	24·2	86·12	9·95	22650	1·91	1·88 (Stu); 1·88 (H).
	95·3	71·40				
Benzene 1st Series	24·8	27·57	27.74			
	95·4	27·92				
2nd Series	23·3	27·02	~~0~~	0	0	0 (Mc & Sm).
	95·1	27·23	27·12			

† See for references under Table III (A).

The negative value of A for acetonitrile has no significance and might have arisen from high values at the ordinary temperature as a result of adsorption effects. The slightly higher polarisation for benzene at the steam temperature is due to experimental errors.

The significance of the values of moments in relation to molecular structure has been discussed by several workers in the past and it is not proposed to go further into that question in this communication. In a

separate paper, to be published shortly, the results of electronic and atomic polarisations will be given and discussed.

Summary.

1. The dielectric coefficients of 16 gases and vapours have been measured at two or three temperatures and the values obtained have been employed in calculating their electrical moments. Cyclopropane, benzene and carbon tetrachloride are definitely nonpolar while all other substances have appreciable electric moments.

2. The compressibility values at the ordinary temperature were determined by studying the variation of refractive index with pressure. Accurate values for substances which are gaseous at the ordinary temperature and pressure and approximate values for substances which are liquids under ordinary conditions, have been obtained.

3. The results of dielectric coefficients obtained in the present investigations have been compared with the existing data by others.

In conclusion my best thanks are due to Professor Sir C. V. Raman, Kt., F.R.S., N.L., for his continued interest in the work.

THE CONDENSATION OF ALDEHYDES WITH MALONIC ACID IN THE PRESENCE OF ORGANIC BASES.

Part V. The Condensation of Anisaldehyde.

By K. C. Pandya

and

Toquir Ahmad Vahidy.

(*From the Department of Chemistry, St. John's College, Agra.*)

Received May 18, 1936.

Condensations of anisaldehyde to give *p*-methoxy-cinnamic, or methyl-ether-*p*-coumaric, acid, have been reported by several workers. Perkin[1] and Eigel[2] heated the aldehyde with anhydrous sodium acetate and acetic anhydride in a sealed tube at 170°and 175°–180° respectively and were among the first to carry out the condensation. Rotarski[3] used the open flask. Knoevenagel, who was the pioneer to use organic bases, tried two different methods. In one, he heated equal molecules of the aldehyde and of malonic acid in the presence of 8% alcoholic ammonia on the water-bath, or a molecular mixture of the aldehyde and of the neutral ammonium malonate in alcohol on the water-bath till the whole was evaporated to dryness.[4] In the other, he used organic bases, *i.e.*, he heated on the water-bath anisal-aniline with malonic acid or with acid aniline malonate[4]; he also heated molecular proportions of the acid and the aldehyde in the presence of about 1/20 mol. of isoamylamine for several hours on the water-bath.[5] The literature contains also reports of condensations of the aldehydes with other reagents whereby the ester was first formed and the *p*-methoxy-cinnamic acid was then obtained by hydrolysing the ester; thus Vorländer[6] and Reychler[7] used ethyl acetate and sodium at 15°, Bunge used ethyl-bromacetate and zinc, and decomposed the product with moist ether[8], and Knoevenagel condensed the aldehyde with ethyl malonate in the presence of diethylamine or piperidine.[9] Every one of these methods took several hours, eight or more, except Knoevenagel's ammonia method which required an hour or two. The yield is often not stated, but there is reason to think that it could not be good. (*Vide* Experimental.)

In 1925, two important methods were reported: Dutt, following the suggested modification of Haworth, Perkin and Rankin,[10] used a mixture of a secondary and a tertiary base, the piperidine-pyridine mixture, and

obtained an 80% yield on about six (?) hours' heating,[11] while Robinson and Shinoda prepared the acid " in almost quantitative yield " by heating the aldehyde, the malonic acid and pyridine (1 : 2·5 : 3 mols.) with a few drops of piperidine, on the steam-bath for 1·5 hours and then boiling.[12] Later on Dalal and Dutt, using molecular proportions of quinoline alone, obtained 72·3% yield on 5 hours' heating.[13] Kurien and Pandya showed that the same condensation in the presence of only a trace of pyridine alone, gave a 78% yield on heating on the water-bath for 4 hours only.[14] In the present paper, it is shown that in the same way other organic bases also help in the condensation, giving good yields, only on about 4 hours' heating. With pyridine, lutidine and iso-quinoline, the product obtained was *p*-methoxy-cinnamic acid; in the remaining cases, however, *i.e.*, with piperidine, quinoline, quinaldine, diethylaniline, dimethylaniline, benzylmethylaniline, *o*-toluidine, *m*-toluidine, acridine and α-naphthoquinoline, the first product obtained was the anisalmalonic acid (*cf.* Knoevenagel, *loc. cit.*), which either on longer heating or on boiling with alcohol, easily changed into the acrylic or cinnamic acid.

It was also found that the condensation to anisylidenemalonic acid could take place, though much slowly, without the presence of a third substance, an observation made also in the cases of salicylaldehyde[15] and of piperonal.[16] Thus the yield, obtained at the end of 4 hours' heating, was a little above 50%, and reached up to about 70% after 14 hours' heating, and to 88% after 24 hours' heating on the water-bath. It is again seen that the base plays the part of a catalyst, shortens considerably the time required for their maximum yield, and need really be present in traces only. Bases like pyridine in larger proportions would obviously help as solvents, and longer or stronger heating would, by itself or in the presence of excess of some bases, remove carbon dioxide and lead to the formation of the unsaturated monobasic acid.

In all the cases examined, the product, as before, is slightly or deeply coloured, but on careful crystallisation the colour usually remains in the alcohol used as solvent, and white crystals are obtained. The melting-point presents some interesting features. Heilbron and Bunbury[17] state that the acid *p*-methoxy-cinnamic exists in two forms, one melting at 170° and the other at 66°. Our acid, as that of all the workers referred to above, was the one with the higher melting-point. It usually melted at 171°, but after a second crsytallisation from alcohol, the melting-point rose to 172–73°. In the literature it is given variously from 170° to 173°·8. Robinson and Shinoda (*loc. cit.*) record 173°. Heilbron and Bunbury also state that the lower-melting readily forms liquid crystals, but say nothing of the kind

for the higher-melting. As a matter of fact, several of the early workers have reported the liquid crystal behaviour of the higher-melting acid, which is also confirmed by us. Thus De Kock found the acid melting at 170°·6 to a turbid liquid which cleared at 185°·5 [18]; Rotarski found the m.p. 170° and the clearing point 185°[3]; Prins found the m.p. 173°·8 and the clarifying point 188°–188°·3[19]; we also found even the purified material, after melting at 172°–73°, go into a turbid state from which it clarified at about 188° or 190°.

Knoevenagel gives the melting-point of anisalmalonic acid as 185°–190°, with strong frothing. Our acid melted at 194° when crude, and when recrystallised from cold alcohol melted at 195°-196° and is identical with that recorded by Boehm[20] (*p*-methoxybenzylidenemalonic acid, m.p. 195°–196°).

It may also be added that Skau and Meier report that the "*f.p* of *p*-methoxy-cinnamic acid is 172°·1, and the transition from the liquid-crystal to liquid-amorphous state is 187°·3".[21] We observed that the acid did not change its melting-point or its behaviour as liquid-crystal, even when it was recrystallised from different solvents like acetone, glacial acetic acid and alcohol.

It would not be unfair to claim that, of all the methods noted above of preparing *p*-methoxy-cinnamic acid from anisaldehyde, those employing traces of certain organic bases like pyridine, iso-quinoline and the like are the best: in point of yield they can compare favourably with the best, namely, that of Robinson and Shinoda, as both give almost quantitative yield: and if the latter method takes less time, our method requires much less materials.

Experimental.

Condensation with sodium acetate and acetic anhydride.—Anisaldehyde was condensed with fused sodium acetate and acetic anhydride, by Perkin's method (*loc. cit.*), using an open vessel, a flask with a reflux condenser, like Rotarski (*loc. cit.*) and maintaining a temperature of 170°–180° for about eight hours. The acid was separated as Perkin did, but the yield was only 20% with a m.p. 171°C.

Condensation with neutral ammonium malonate in the presence of alcohol.—Anisaldehyde (1·3 g.) and neutral ammonium malonate (1·4 g.) were mixed and covered over with alcohol. The whole was evaporated on a water-bath to dryness, according to Knoevenagel.[4] After treatment with sodium carbonate solution and dilute sulphuric acid the acid was separated. According to Knoevenagel, the acid should be the dibasic anisylidenemalonic acid, melting at 185°–189° C. The acid actually obtained

was, however, the corresponding acrylic or the *p*-methoxy-cinnamic acid, melting at 170° when crude, and at 171° when warmed with alcohol and crystallised out of the solvent. The yield was 45%.

Condensation with malonic acid in the presence of traces of organic bases.—These condensations were carried out as before.[16] Anisaldehyde (Schering-Kahlbaum, pure, 2·7 g., *i.e.*, 1/50 mole.) was mixed with the same molecular proportion of malonic acid (2·08 g., Schering-Kahlbaum's, pure "for scientific pruposes", and dried at 100°–110° C.). The base was throughout in 0·07 mol., as detailed in the table below. The mixture was kept on a water-bath with a reflux condenser, for 4 hours. The progress of the reaction was very well indicated by the formation of a solid, variously, and often beautifully, coloured; after 4 hours' heating, the mass was left in the flask overnight, then treated with sodium carbonate solution, warmed, filtered from any adhesive resinous matter, and then treated with hydrochloric acid. The acid was precipitated, filtered, dried and recrystallised from alcohol. The lowest yield was 56%, in one case, but ranged usually from about 80 to 98%.

The following bases were tried:—Pyridine, piperidine, lutidine, quinoline, iso-quinoline, diethylaniline, dimethylaniline, benzylmethylaniline, *o*-toluidine, *m*-toluidine, acridine and α-naphthoquinoline. (*Vide* Table I below.)

Condensation with malonic acid without any base or any other reagent.—This was set up in the same way. One lot showed that, not only the condensation occurred without the presence of a base or of any other reagent, but the yield after 4 hours' heating was better than was obtained by Perkin's or by Knoevenagel's method, being about 52%. Another lot was heated on the water-bath for 14 hours and gave an increased yield of about 70%. A third lot, maintained on the water-bath for 24 hours, gave a still greater yield of a little less than 90%.

That the duration of heating has an important effect in this condensation was also illustrated by the fact that when one lot was heated with the usual trace of pyridine alone for 2 hours instead of 4, the yield was about 45% only. Similarly in the condensations brought about in the presence of some other bases, the final yield is likely to improve with slightly longer heating. In this case, as already stated, longer heating also splits off CO_2 and gives the methoxy-cinnamic acid.

In the following table the yields as obtained are given. It may be noted that in the first three cases the acid *p*-methoxy-cinnamic was obtained; in the last—condensation without a base—a mixture of the cinnamic and

malonic was obtained; while in the remaining cases, the anisalmalonic acid was obtained alone, under the conditions of the experiment.

TABLE I.

Base	Amount used	Yield in grams	Yield %	Nature of product
Isoquinoline ..	0·18 c.c.	3·5	98·3	—Cinnamic
Lutidine ..	0·15 ,,	3·0	84·3	,,
Pyridine ..	0·115 ,,	3·0	84·3	,,
Acridine ..	0·25 g.	3·5	78·8	—Malonic
Benzylmethylaniline ..	0·24 c.c.	3·2	72·07	,,
Diethylaniline ..	0·19 ,,	3·5	78·8	,,
Dimethylaniline ..	0·18 ,,	3·0	67·5	,,
α-naphthoquinoline ..	0·3 g.	3·5	78·8	,,
Piperidine ..	0·12 c.c.	3·2	72·07	,,
Quinaldine ..	0·2 ,,	3·5	78·8	,,
Quinoline ..	0·18 ,,	3·5	78·8	,,
o-toluidine ..	0·16 ,,	2·8	63·06	Resin also
m-toluidine ..	,, ,,	2·5	56·3	,,
Without any base ..	4 hours	2·3	51·8	Mostly Malonic
	14 ,,	2·8	about 70·0	Mixid acids
	28 ,,	3·5	,, 87·5	,,

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THE CONDENSATION OF ALDEHYDES WITH MALONIC ACID IN THE PRESENCE OF ORGANIC BASES.

Part VI. The Condensation of *p*-Hydroxybenzaldehyde.

By K. C. Pandya
and
Toquir Ahmad Vahidy.
(From the Department of Chemistry, St. John's College, Agra.)

Received May 25, 1936.

The condensations of *p*-hydroxybenzaldehyde with malonic acid in the presence of traces of various organic bases are comparable with those of salicylaldehyde on the one hand[1] and with those of anisaldehyde on the other.[2] There is, however, little work done previously on the condensation of *p*-hydroxybenzaldehyde.

Tiemann and Herzfeld, as early as 1877, applied Perkins' reaction to this aldehyde, but first changed it into the sodium derivative, the *p*-aldehyde-sodium-phenolate being then heated with dehydrated sodium acetate and acetic anhydride.[3] Eigel used the aldehyde itself in the same way, about ten years later.[4] The product was the *p*-acetoxy-cinnamic acid, from which the *p*-hydroxycinnamic, or *p*-coumaric, acid was generated by decomposing it with hot alkali. Zincke and Leisse heated the mixture of the three, taken in 0·8 : 2 : 3 mol. proportions, on a sand-bath for 4-5 hours, hydrolysed the separated acetyl-*p*-coumaric acid by boiling with alkali and then precipitated the acid by acidifying with HCl.[5] From the note left by Dutt[6] and the absence of any account of it in the paper, one must conclude that the pyridine-piperidine mixture was not successful in bringing about the condensation of the aldehyde with malonic acid. With molecular quantities of quinoline, however, later on, Dalal and Dutt record an yield, after 10 hours' heating, of 10·6%, as "the best possible yield."[7] Later on Kurien and Pandya, on condensing this aldehyde with malonic acid, in the presence of about 0·5 mol. of pyridine alone, obtained a more satisfactory yield of 33% of *p*-hydroxycinnamic acid.[8]

In examining the effect of varying different conditions of the condensation, we find in the present paper that the yield again doubles, increases to over 64%, by slight alterations in the proportions of the base. Lutidine and acridine also give an equally good, *i.e.*, 64·03 per cent. yield in 0·3 and 0·15 mol. proportions respectively. A few other bases that were tried gave

yields that were below 60%, but not less than 30%. It is probable that in these cases too, adjustments in conditions may be found out whereby still better yields may be obtainable.

In comparing the results of ortho- and para-hydroxybenzaldehydes, it is evident that the yields in the case of the latter are all lower. This may be due either to the nature of the aldehyde itself, or to the fact that the molecular proportions of each base used with salicylaldehyde are much smaller than those in the other case, or may be due partly to one and partly to the other.

Comparing the results with those of the condensations with the methyl-ether of *p*-hydroxybenzaldehyde, *i.e.*, anisaldehyde,[2] one gets a better basis of comparison, so far as the bases were used, in the cases of both the aldehydes, in practically the same proportions. The yields in the cases of the anisaldehyde-condensations are, however, immensely higher, the lowest being 56%, almost equal to the highest of the hydroxy-aldehyde, and the highest being the theoretical. This can only be understood to be due to the methoxy-group in the one case and the unsubstituted hydroxy in the other.

Investigations, that are planned, into a similar study of the *o*-methoxy-benzaldehyde, and comparison with the case of salicylaldehyde might probably throw more light.

There is one more point of interest. In the case of anisaldehyde the heating on water-bath was for 4 hours which sufficed for the high yields: in the present case 8 hours' heating was necessary to obtain the reported yields.

A condensation was set up as usual without any base or any other reagent under the usual conditions. At the end of eight hours, the yield was 15%.

The formation of resin in these condensations, giving low yields, indicates some other reaction like polymerisation taking place also between the aldehyde molecules.

The condensation was also carried out under conditions similar to those employed by Robinson and Shinoda in their preparation of *p*-methoxy-cinnamic acid,[9] *i.e.*, the aldehyde, the acid and pyridine were taken in the ratio of 1 : 2·5 : 3 mols., with a few drops of piperidine also, were heated on the water-bath for 1·5 hours and then boiled on the free flame for about 10 minutes. The yield was, however, 60%.

Experimental.

The condensations were carried out in the usual way with the base ranging from 0·15 to 0·3 mol. Thus 2·5 gm. of the aldehyde, 2·0 gm.

of dried malonic acid and 0·25 c.c. of pyridine were heated under reflux on the water-bath at 100° for 8 hours, and left overnight[2]. The product being treated with sodium carbonate solution, warmed, filtered and acidified with concentrated HCl, the coumaric acid was precipitated. On purification it melted at 206–7°. *Compare*, Tiemann and Herzfeld, 206° (*loc. cit.*). Will gives 207°, decom.,[10] and Power and Moore found it to be 210–213°.[11]

In addition to a condensation without a base, and another with the pyridine-piperidine mixture (according to Robinson and Shinoda), the following single bases were tried: pyridine, piperidine, lutidine, quinoline, iso-quinoline, quinaldine, cinchonidine, acridine, α-naphthoquinoline, benzylmethylaniline, diethylaniline, dimethylaniline and collidine.

TABLE I.

Name of the base	Mol. proportion	Yield gram	Yield p.c.
Pyridine	0·15	2·1	64·03
Piperidine	0·25	1·8	54·7
Lutidine	0·3	2·1	64·03
Quinoline	0·3	1·7	51·8
Iso-Quinoline	0·3	1·6	48·8
Quinaldine	0·3	0·8	24·4
,, ...	0·15	1·0	30·5
Cinchonidine	0·15	1·5	45·7
Acridine	0·15	2·0	60·9
α-Naphthoquinoline	0·15	1·8	54·7
Benzylmethylaniline	0·15	1·8	54·7
Diethylaniline	0·15	1·5	45·7
Dimethylaniline	0·15	1·3	39·6
Collidine	0·15	1·0	30·5
Pyridine + Piperidine	3·0+0·25	2·0	60·9
No Base		about 0·5	15·0

In every case the product was *p*-hydroxycinnamic acid, or the *p*-coumaric acid, alone.

The condensations were first started by Messrs. P. N. Kurien and Azhar Ali Khan. Thanks are also due to the Government of the United Provinces for the grant of a research scholarship to one of us (T. A. V.) which has enabled him to join in this work.

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THE CONDENSATION OF ALDEHYDES WITH MALONIC ACID IN THE PRESENCE OF ORGANIC BASES.

Part VII. The Condensation of *m*-Hydroxybenzaldehyde.

By K. C. Pandya
and
Toquir Ahmad Vahidy.
(From the Department of Chemistry, St. John's College, Agra.)

Received May 25, 1936.

The condensations of *m*-hydroxybenzaldehyde are comparable with those of salicylaldehyde[1] and of *p*-hydroxybenzaldehyde.[2] They could also be compared with those of *m*-methoxybenzaldehyde which it is hoped to study at an early opportunity.

As in the case of the *p*-hydroxybenzaldehyde,[2] these condensations also have not been so well studied. Tiemann and Ludwig in 1882[3] and Rieche in 1889[4] applied Perkin's reaction by heating the aldehyde, sodium acetate and acetic anhydride (1 : 2 : 4 parts) for 4–5 hours ; the acetyl-*m*-coumaric acid so obtained was hydrolysed with hot alkali, and thus the *m*-hydroxycinnamic, or *m*-coumaric, acid, was obtained. As in the case of the *p*-isomer,[2] the condensation with malonic acid in the presence of the pyridine mixture of Dutt, did not go, and the first reference of the condensation with malonic acid is found in Dalal and Dutt's paper,[5] where a 70% yield is recorded when the *m*-hydroxybenzaldehyde was heated with malonic acid for 10 hours at 80–85° in the presence of molecular amounts of quinoline.

Wondering whether the method of Kurien and Pandya,[6] if applied to this case, would result in any improvement of the good yield reported by Dalal and Dutt, experiments were started exactly as in the case of the *p*-isomer. The first experiment conducted by Kurien and Azhar Ali Khan in this laboratory, with small amounts of pyridine alone, gave at once an almost theoretical yield (95%), but, very strangely, when quinoline was tried, there was apparently no reaction. Isoquinoline again gave a 62·5% yield, but lutidine gave only 10%, and a few other bases, again failed each to give any solid product.

When the work was started by us, it was observed that at the water-bath temperature as well as at lower (80°) temperatures, the yields were very

poor or nil. But on conducting the condensation at 105–110° for 8 hours, much better yields were obtained. This was found to be the optimum temperature with 0·15 mol. of the organic base, as higher temperature than 110° did not improve, but rather diminished, the yield.

In this way pyridine gave 100% yield, Robinson and Shinoda's method[7] gave 91·4%, and some other bases also gave very satisfactory yields (*see* Table I below).

TABLE I.

Name of the base	Mol.	Yield gram	Yield p.c.
Pyridine	0·15	3·3 nearly	100·0
Piperidine	0·15	2·4	73·2
Lutidine	0·3	2·7	82·3
Quinoline	0·15	2·0	60·9
Iso-Quinoline	0·15	2·7	82·3
Quinaldine	0·15	2·1	64·03
Cinchonidine	0·15	1·5	45·7
Acridine	0·15	2·0	60·9
α-Naphthoquinoline	0·15	2·0	60·9
Benzylmethylaniline	0·15	1·5	45·7
Diethylaniline	0·15	1·3	39·6
Dimethylaniline	0·15	1·0	30·5
Collidine	0·15	1·3	39·6
Pyridine+Piperidine	3·0+0·15	3·0	91·4
None	..	0·0	0·0

Comparing with the yields obtained with the other two isomeric aldehydes, it is obvious that some of the bases have given best results with the meta-isomer. But there is no uniformity such as may permit a genreralisation. For example, when no base is used, the meta-benzaldehyde gives no

yield at all, even when heating is prolonged, while the *o*- and the *p*-isomers show appreciable condensation each.

Experimental.

The procedure was exactly the same as applied to *p*-hydroxybenzaldehyde, each experiment being performed with 1/50 mol. of the aldehyde and the malonic acid, and the base being usually in the ratio of 0·15 mol. to 1 of each of the other two. The temperature was always 105–110°, and the heating was for 8 hours.

The acid in every case of condensation was the *m*-coumaric, or *m*-hydroxy-cinnamic.

It can be seen that this method of preparing the coumaric acid, not only gives a very high yield, but gives it in a straightforward way, without the intermediary of the acetylated acid or of long heating in sealed tubes, as in Perkin's reaction.

The experiments were first started by Messrs. P. N. Kurien and Azhar Ali Khan.

Thanks are also due to the Government of the United Provinces for the grant of a research scholarship to one of us (T. A. V.) which has enabled him to take part in this work.

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